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TEXTILE RESEARCH JOURNAL

Nylon 6—Current Developments[1]

G. A. Nesty

Allied Chemical Corporation, New York 6, New York

Abstract

Epsilon polycaproamide (nylon 6), with more than twenty years' effort behind it in Europe, is now established as a commercial fiber in the U.S. Historically, its development goes back at least sixty years, when it narrowly missed becoming the first truly man-made fiber. Although the molecular structure of nylon 6 is almost identical to that of nylon 6,6, its melting point is lower, probably due to special entropy considerations. Thus nylon 6 permits easier and more economical thermal processing. Thermal properties of the two nylons, even when both are modified with antioxidants, are seen to be similar in many respects, but the 6 type has more resistance to thermal creep at high loads and is more stable with respect to end-group changes. A major domestic producer has developed technology solving the old problem of excessive monomer content without resorting to washing of yarn. Properties, applications, and current developments of various forms of nylon 6 fibers are described. A large potential is shown to exist for expanded use of this versatile fiber.

Commercial Production of Nylon 6

Thermal Behavior Considerations

Although the history of nylon 6 goes back some 60 years, its initial commercialization was in Germany, where it was largely channeled into military applications during World War II. With the restoration of peace in 1945, development of nylon 6 fiber production technology advanced rapidly, and plants were erected in many parts of the world, until today there are at least 30 producing type 6 polyamides. Most of the nylon hosiery now being made in Europe, for example, utilize nylon 6, and the finer textile deniers in various lusters, as well as staple, have been developed to a high degree. In our own country, availability of nylon 6 fiber in commercial quantities is a fairly recent development, which has inspired much interest in differences relative to the established domestic 6,6 product. In fact, the new product was forced to overcome several somewhat unsatisfactory experiences with samples of early Perlon yarn. Consideration of a specific nylon 6, Caprolan,[2] will help clarify the differences between nylon 6 and 6,6. Properties of polyamide yarns are composite results of numerous parameters in monomer purity, polymerization, and spinning process. Therefore ultimate yarn products from the same basic monomer may differ greatly. Early in the development of Caprolan it was recognized that drawbacks associated with commercial nylon 6 of that time were not inherent in the polyamide itself but were a result of imperfect choice of processing conditions. Therefore, in the development of Caprolan, new processes were chosen which would unmask the inherent ability of nylon 6 molecular struc-

[1] Presented at the 29th Annual Meeting of Textile Research Institute, New York City, March 24, 1959.

[2] Allied Chemical's polyamide fiber trademark.

ture. The lower melting point of the 6 product attracted much interest; this difference influences thermal properties of nylon 6 in general at levels well below the melting point, and was experienced with early Perlon. The situation in the case of Caprolan can be described graphically by plotting degree of retained tenacity against temperature, measured on specimens in contact with a slightly convex heater-block mounted on the Scott IP-4 tester. These changes in tenacity are reversible.

In Figure 1 both specimens are commercially dipped-and-stretched tire cords made from heat-stabilized yarns. Essentially similar conditions obtain when stabilized or unstabilized yarns are tested, provided polymer viscosities, yarn tenacities, etc. are comparable for the two materials. It is obvious that the plasticizing effect of heat on both materials is essentially the same down to the 50% retention level of original tenacity, which is generally accepted as a safe engineering limit. After this point, the rate of strength reduction becomes more rapid in the nylon 6 as it approaches its melting range, but since both materials are then down below half their original strength, the differences become academic.

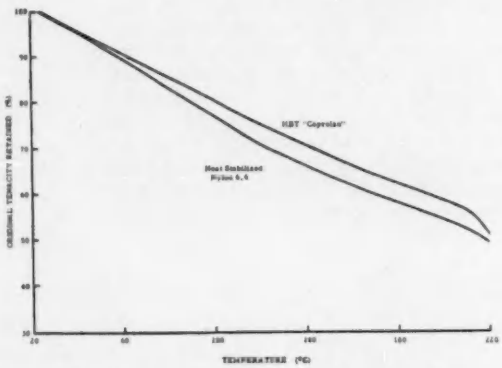

Fig. 1. Commercially tensilized tire cords.

Likewise, considerable attention has been focused on resistance to thermal degradation. Heat-stabilized HBT Caprolan is modified to such an extent that 24 hr. exposure in air at 165° C. results in a breaking-strength loss of less than 10%, which was outstanding at the time of its inception (September 1956). This compares to losses of from 35 to 80% for unstabilized nylon yarns. Strength retention of this yarn, compared with that of the more recently developed nylon 6,6 types when exposed to air at various temperatures for periods of up to 5 weeks, is seen in Figures 2 and 3. Elapsed time is plotted on a log scale for convenience in presenting these data.

"Zero Strength" Temperatures

Both creep and oxidation phenomena participate in behavior of the improved nylon 6 yarn in a test technique designed to measure "zero strength" temperature. This is the effective melting point as determined by measuring the temperature at which the yarn breaks under a nominal load (100 g.) when the temperature is raised 1° C./min. from an initial temperature of 190° C. Such tests indicate that the stabilizer raises the effective melting point of the yarn by 15–20° C. Unstabilized yarn breaks at about 215° C. versus 231° C. for 840-den. HBT Caprolan. Hill [13] has noted that the nylon 6,6 melting point is 8–16° C. lower in air than in nitrogen. This higher effective melting temperature of stabilized Caprolan is further paralleled by the relative performance of Caprolan tire and cord versus

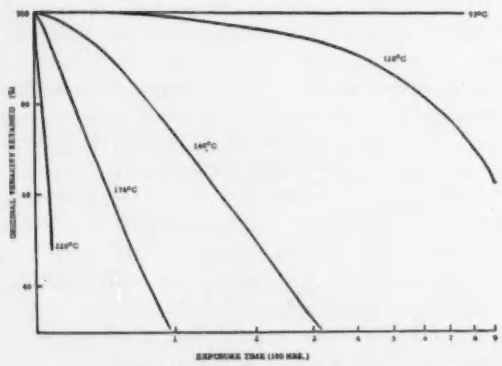

Fig. 2. HBT Caprolan.

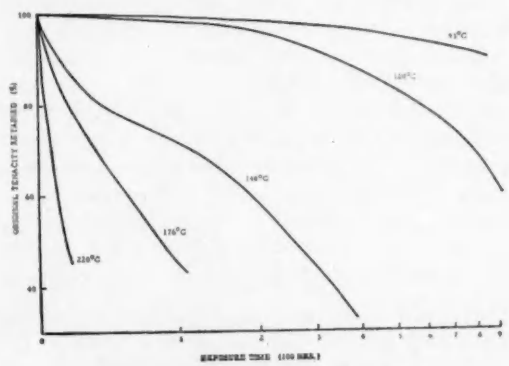

Fig. 3. Heat stabilized nylon 6,6.

German unstabilized Perlon cord during tensilizing. Whereas the latter tends to burn out at temperatures exceeding 210° C. [19], Caprolan tire cord can be tensilized at temperatures of 224° C. for residence times up to 30 sec., without evidence of tensile strength degradation.

When the same technique (but with increasing pre-loads) is used, the breaking temperature (thermal load index) exceeds that of nylon 6,6. For example, with an initial load of 2.50 Kg., the 6 yarn breaks at 219° C. versus 203° C. for the 6,6 yarn. In a series of studies made using various loads, with initial temperatures of 190° C. for loads below and 150° C. for loads above 2.5 Kg., thermal load index temperatures were determined and plotted as shown in Figure 4.

This graph shows a cross-over point about 1900 g., which demonstrates that HBT Caprolan has a greater resistance to high temperature creep at the higher loads. The protective effect of the stabilizer system in the HBT is dramatized by the inclusion of a T.L.I. curve for unstabilized HB Caprolan.

Thermal Creep Failure

Another approach to evaluation of the ability of materials to demonstrate reduced secondary creep under rather high loads, while subjected simultaneously to thermal stress, has been proposed, based on measurement of time-to-break. Hot-load testing of greige tire cords is carried out in a closed circulating air oven. Single cords are loaded with 6.8 Kg., and the times to failure at oven temperatures of 160, 170, and 180° C. recorded. Results are shown in Figure 5.

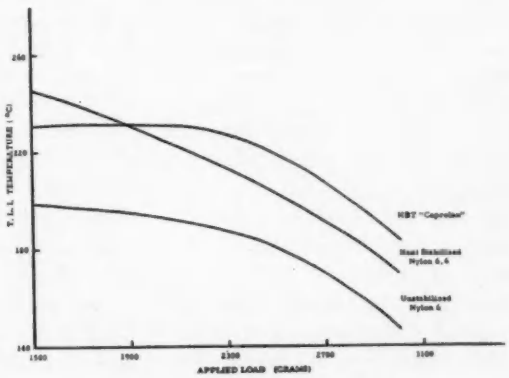

Fig. 4.

Molecular Structure

The fact that a difference in melting points of 6 and 6,6 exists at all has been the subject of considerable speculation. It cannot be explained on the basis of molecular structure, since the two polymers are structurally almost identical and are actually isomeric. Although the adjoining segments of the 6,6 chain are derived from the diamine and the carboxylic acid in regular alternating order, the nylon 6 chain built up from the opened rings consists of alternating isomeric segments, and it has been noted that only the transposition of every other oxygen and two hydrogen atoms would be necessary to achieve the same arrangement as in the 6,6 polyamide, or vice versa, as shown in Figure 6.

Density of hydrogen bonding of molecular layers of crystallites in 6 polymer has been supposed to be subject to an unfavorable spacing of amide groups, as noted in Figure 7A, lending support to an explanation of its lower melting point.

The x-ray structural analyses of Bunn and coworkers [15], however, have established inversion of

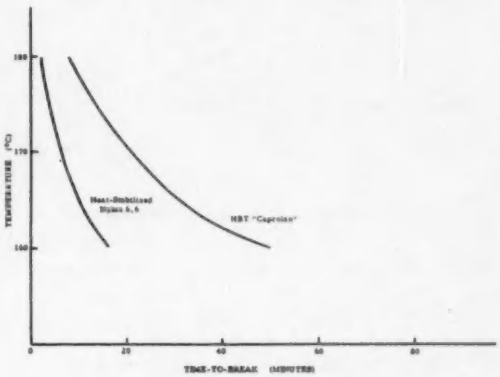

Fig. 5. Greige tire cords; 6.8-Kg. load.

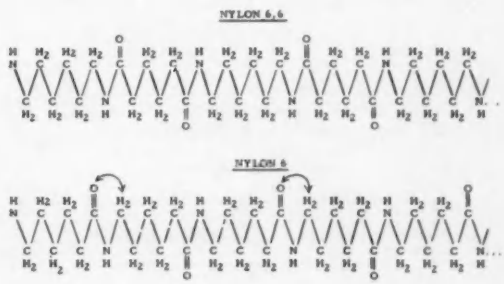

Fig. 6.

alternate chains in nylon 6, thereby making all the hydrogen bonds as shown in Figure 7B. This inversion is not required for the nylon 6,6 to make all of its hydrogen bonds. This structural difference may account for the 50° C. difference in melting point of nylon 6 (215° C.) and nylon 6,6 (265° C.).

The fusion temperature T_f is related to the heat of fusion ΔH_f and entropy of fusion ΔS_f through the equation

$$T_f = \frac{\Delta H_f}{\Delta S_f}$$

If one assumes that ΔH_f values for the two similar nylon forms are reasonably close together, as shown by Dole and coworkers [17], the difference in T_f values arises from substantial differences between entropy of fusion [10].

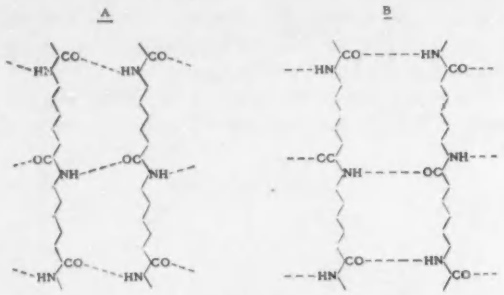

Fig. 7.

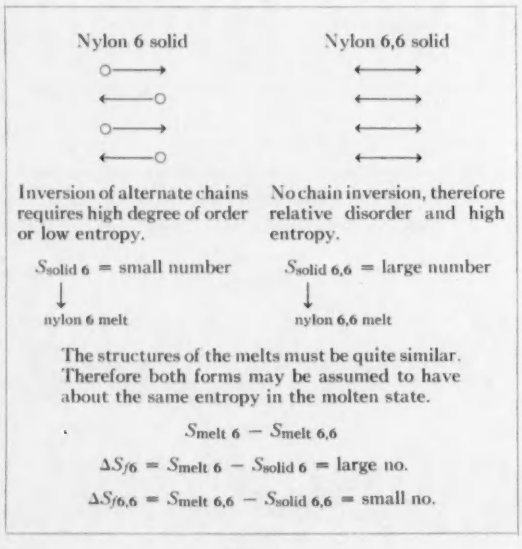
Nylon 6 solid
Nylon 6,6 solid
Inversion of alternate chains requires high degree of order or low entropy.
No chain inversion, therefore relative disorder and high entropy.
$S_{solid\ 6}$ = small number
$S_{solid\ 6,6}$ = large number
nylon 6 melt
nylon 6,6 melt
The structures of the melts must be quite similar. Therefore both forms may be assumed to have about the same entropy in the molten state.
$S_{melt\ 6} - S_{melt\ 6,6}$
$\Delta S_{f6} = S_{melt\ 6} - S_{solid\ 6}$ = large no.
$\Delta S_{f6,6} = S_{melt\ 6,6} - S_{solid\ 6,6}$ = small no.

Fig. 8.

One may in fact generalize with the assertion that low entropies of fusion are usually associated with high melting points of polymers [16].

In the present instance, the possible entropy relationships are demonstrated with the aid of the schematic representation shown in Figure 8. Therefore the low entropy of fusion of 6,6 compared with that of 6 results in a higher melting point for the former.

Thus it appears that the difference in melting point is due to a special entropy consideration, and that once solidified, the two polymers are almost alike in molecular structure and thermodynamic properties. This reasoning accounts for the fact that similarities in thermal behavior of the two materials in general overshadow the actual levels of the melting points themselves. Some second order differences remain, however, and these enter into the economic aspects of such commercial operations as hot-stretching, texturizing, and fabric heat-setting, where generally lower temperatures may be used with nylon 6. This affords users of nylon 6 significant savings in power consumption. The same principle applies to fiber production, making possible a lower spinning temperature, with consequent reduction in thermal degradation in the melt.

Depolymerization

Another area of interest in connection with the response of nylon 6 to continued application of heat relates to monomer reversion. This has been studied by tests conducted both in circulating air and in vacuum, with a nitrogen sweep.

It is well recognized from the literature that nylon 6 in the melt state tends to set up a polymer–monomer depolymerization–repolymerization equilibrium leading to polymer containing 6–10% free monomer in equilibrium with the polymer along with minor amounts of low cyclic polymers. Monomer regeneration studies on 840-den. HBT Caprolan were made at temperatures of 150° C. and 185° C. both in air and partial vacuum (nitrogen at 10 mm. Hg) for time periods ranging up to 3 weeks. Monomer regeneration as measured by weight losses indicated that at 150° C. in air or vacuum the 840-den. HBT Caprolan exhibited only slight reversion to monomer. After 21 days, total maximum weight losses were about 2.5%, of which about 1% was spin finish. Loss rates were accelerated at 185° C., but the stabilized forms of 6 and 6,6 behaved in approximately the same manner. Figures 9, 10, 11, and 12 show

the comparative weight losses versus time for 840-den. HBT Caprolan versus stabilized and unstabilized nylon 6,6.

These graphs show that heat stabilized Caprolan and heat stabilized nylon 6,6 give more or less equivalent degradation losses. Both stabilized yarns are definitely superior to the unstabilized nylon 6,6 sample. These latter results are not unexpected, since polyamide degradation is strongly accelerated by the presence of oxygen, and the stabilized yarns have been to some degree protected against oxidative effects.

Effects of Steam

Further, Meacock [18] has shown that the stability of 6 polymer with respect to end groups is superior to that of 6,6 polymer when held at 293° C. under atmospheric pressure of steam. Washed 6 polymer shows an initial drop in relative viscosity owing to development of its equilibrium lactam content. However, the overall stability of the 6 polymer, as shown in Figure 13, is in marked contrast to the changes in 6,6 polymer in Figure 14.

The continued increase in amino end-group content in the 6,6 polymer after about 12 hr., while carboxyl end-group content and relative viscosity remain nearly constant, is indicative of the formation of secondary amino groups within the chain. Such groups may lead to cross-linking and gel formation. Visual observation has shown the extent of gelling in 6,6 polymer to be large in comparison with 6 polymer [18].

Nylon 6 in the United States

Development of Caprolan

What then are the general process considerations which account for the enhanced thermal endurance of Caprolan nylon 6? Although German work had indicated that high tenacity yarns could be prepared from nylon 6, these yarns had generally inferior properties, by American standards.

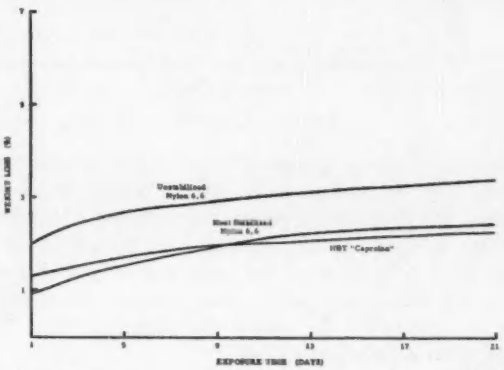

Fig. 9. Vacuum oven, 150° C.; nitrogen at 10 mm. Hg.

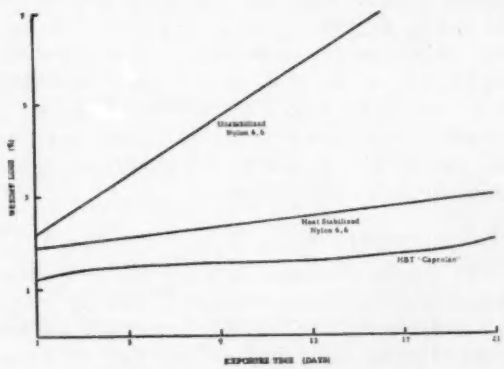

Fig. 10. Air circulating oven; 150° C.

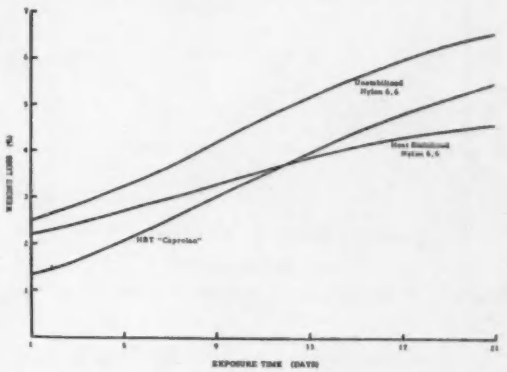

Fig. 11. Vacuum oven, 185° C.; nitrogen at 10 mm. Hg.

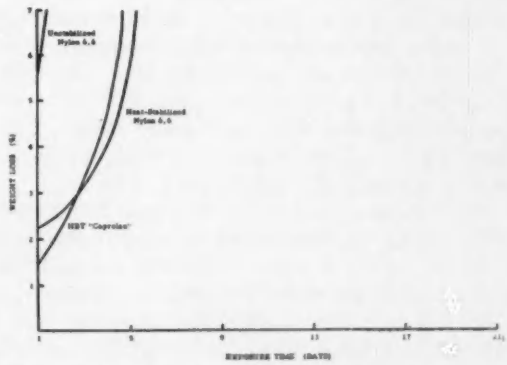

Fig. 12. Air circulating oven; 185° C.

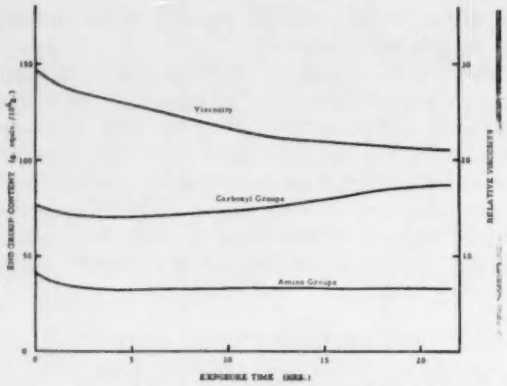

Fig. 13. Washed 6 polymer under atmospheric pressure of steam at 293° C.

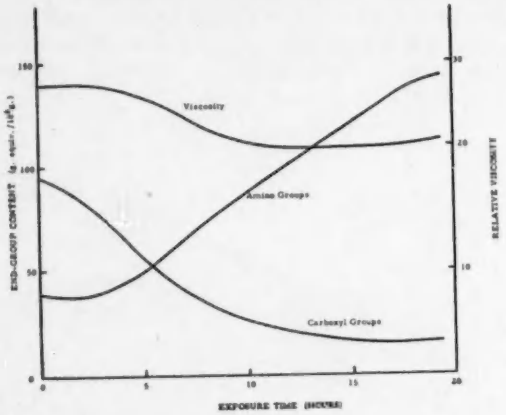

Fig. 14. 6,6 polymer under atmospheric pressure of steam at 293° C.

Some of the deficiencies were attributable to the high monomer content generally encountered in normal German practice, wherein conditions imposed in the spinning process resulted in partial re-equilibration and in regeneration of 4–5% monomer. This required removal by washing, resulting in a high elongation, low modulus, high creep material which was also pervaded with microscopic voids. This latter step was, however, beneficial in improving the elevated temperature characteristics of the yarn.

The Caprolan process was developed along lines which would minimize monomer regeneration and molecular weight changes. Typically the spinning process causes less than 1% change in solution viscosity and molecular weight of the polymer and provides yarns with less than 1.5% extractables content.

Yarn produced in this manner was found to be

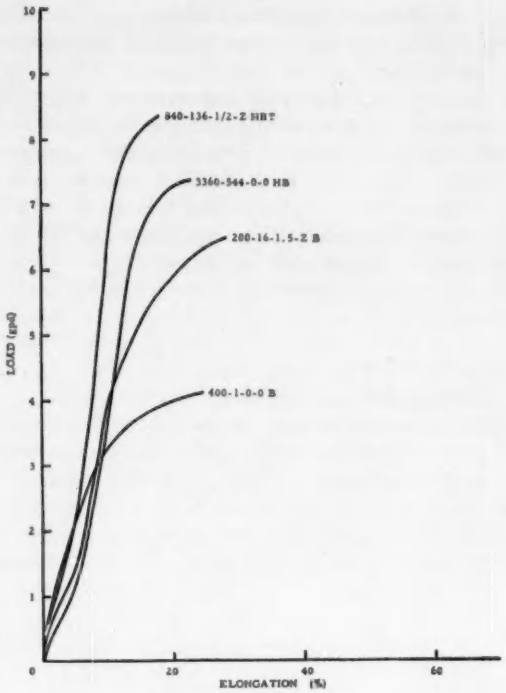

Fig. 15. Caprolan.

capable of being converted to industrial type yarns wth high tenacities, good stretch resistance, low creep and good elastic recovery properties. As with other synthetic yarns, its final fiber properties are not only a function of the molecular weight of the initial polymer used but are very strongly dependent upon the extent to which the undrawn yarn is stretched during processing.

This behavior is not surprising, following the general pattern established by other polyamides. Studies by Dusenbury [8] on tensional, bending, and torsional moduli of monofilaments of 6 and 6,6 produced at various draw ratios showed essentially similar response. Both fibers exhibited virtual independence of torsional modulus from degree of drawing, with the 6 fiber showing very slightly increasing values as draw ratio increased.

Physical Properties

The tensile properties of Caprolan yarns have shown consistent improvement in the past few years, and confident expectation is that considerable further potential exists. Experimental fibers have been produced with tenacities of over 10 g./den., with cor-

respondingly improved visco-elastic properties, and other advances are in the making. Table I lists typical average values for Caprolan in various forms.

Typical load–elongation curves for some of these yarns are shown in Figure 15.

Improvements in Nylon 6

In spite of the lead held by producers of nylon 6,6 when nylon 6 became commercially available in the U. S., many areas for possible improvement in the functional properties of polyamide fibers remained unexploited. The pioneering work of our company in modification of polymers to provide vastly improved thermal properties has already been dealt with. Nylon 6 fibers produced with or without modifiers under conditions which confer the properties described have a number of other interesting characteristics.

Crystallinity

As in other polyamides, many of the properties of nylon 6 fibers are related to degree of crystallinity. Interest in this factor has led to the development of a new x-ray technique which provides a means of determining crystallinity on a percentage basis. Flock prepared from the fibers to be measured is compressed into a dense pellet with a special ram type mold. This specimen is placed directly in the x-ray beam, and the diffraction is recorded on a photographic plate which is kept rotating during the entire exposure period. The combination of the short lengths of fiber, their random orientation in the specimen, and the rotating plate gives a diffraction pattern of crystalline intensities uniformly dispersed into definite bands. The gamma of the developed film is measured radially with a photodensitometer, and the band profile is plotted from the center outward. A curve for the amorphous regions is obtained by irradiating a specimen of molten polymer in a specially designed cell, recording on film, measuring densities, and plotting as before. Typical curves for nylon 6 are shown in Figure 16. The crystalline and amorphous patterns from which they were plotted, and an example of a

TABLE I. Average Physical Properties of Caprolan

	Regular tenacity Bright (B)			High tenacity Bright (HB); Bright, heat stabilized (HBT)		
	Multi-filament	Mono-filament	Staple	Textile and industrial yarns up to 840 den.		Heavy yarns
Properties	200 den. B	400–4200 den. B	6–15 den. B	560 den. HB	840 den. HBT	2100–15,000 den. HB
Tenacity, g./den.						
Std.	6.7	4.0	3.9*	7.3	8.4	7.4*
Wet	5.4	3.8	3.7*	6.3	7.6	6.6*
Std. loop	5.8	2.8	3.1*	5.7	7.0	6.3*
Std. knot	4.8	3.3	—	5.2	6.3	5.5*
Tensile strength, p.s.i.	98,000	58,000	57,000	106,000	122,000	108,000*
Elongation at break, %						
Std.	28	29	37*	20	18	23*
Wet	32	33	44*	24	22	27*
Maximum extension at zero time for minimum of 99% elastic recovery, 0.017 cycles/sec., %	4*	4*	—	8*	8*	8*
Stiffness, g./den.	24	14	11	36	48	33
Average toughness	0.94	0.58	0.72	0.73	0.73	0.83
Specific gravity	1.14					
Moisture regain	4.5% at standard conditions					
Water absorbency	7.8% at 95% RH					
Melting range	212–220° C.					

* Tensile data presented as typical lot averages, determined on Instron Tester at 100% extension/min. All other tensile data from tests on Scott IP-4, both at standard conditions. Melting range determination made with Fisher-Johns apparatus.

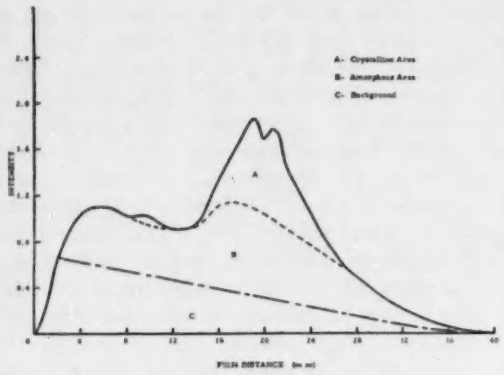

Fig. 16. Crystallinity.

Fig. 17. Top left: amorphous band. Pattern obtained by irradiating molten polymer specimen. Top right: Crystalline bands. Pattern obtained by irradiating random flock pellet and recording the diffraction pattern on a rotating photographic plate. Bottom: Standard x-ray diffraction. Pattern obtained from specimen of parallel fibers and stationary flat plate camera.

conventional diffraction pattern, are presented in Figure 17.

The random spots noted in the amorphous pattern (the left half of Figure 17) are due to diffraction introduced by mica windows in the specimen cell.

These two curves, when superimposed, give an indication of the degree of crystallinity. Before calculating the percentage, however, a blank is run to obtain a curve representing all incoherent scatter, and the area under this curve is subtracted from the total area under the crystallinity curve. The simple calculation

$$\frac{A}{A+B} \times 100 = \% \text{ Crystallinity}$$

is self-explanatory.

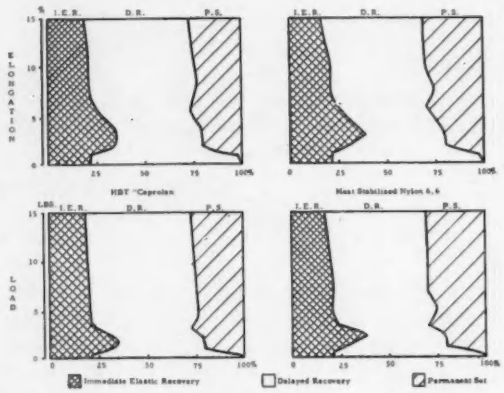

Fig. 18. Recovery behavior of greige tire cords; one cycle (zero time).

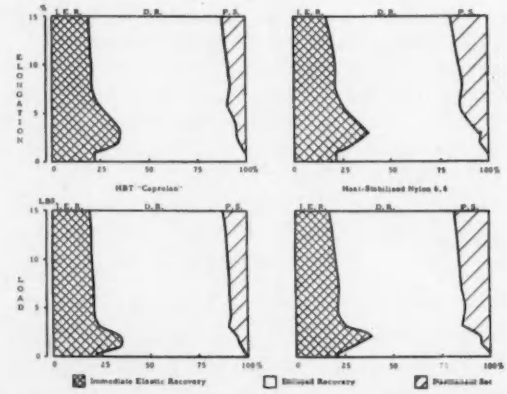

Fig. 19. Recovery behavior of greige tire cords; two cycles (5-min. intervals).

A typical value for high tenacity Caprolan is 30%. This is only slightly lower than comparable 6,6 yarns, which average 31–32%, and represents considerable improvement over earlier efforts, paralleling improvements in tenacity. This method of measurement does not take into account such aspects of crystalline structure as relative proportions of stable and unstable forms, but serves as a useful tool in making quick comparisons.

Elastic Recovery

Visco-elastic properties have been studied by various methods, including that described by Susich and Backer [22]. The recovery behavior of greige tire cords, graphically represented in this manner, indicates that permanent set of the nylon 6 cord is lower than the corresponding values for a comparable 6,6 nylon cord, when measured at zero time or after two cycles with a 5-min. interval. This is seen in Figures 18 and 19, where immediate elastic recovery is shown by the cross-hatched area, delayed recovery by the clear area, and permanent set by the diagonally shaded area.

The principal difference in results obtained by the two cycle method is a reduction in found values for permanent set, showing the "conditioning" effect of the first cycle followed by the 5-min. delay. Ratios of immediate elastic recovery and permanent set for the two polyamides are listed in Table II.

It will be noted that immediate elastic recovery characteristics of the two cords are essentially similar. However, the 6,6 cord exhibits measurably greater permanent set at nearly all tested levels of both load and elongation, especially after double cycling. Investigations are under way to determine what bearing these factors may have on tire growth and flat-spotting behavior.

Hysteresis

Hysteresis behavior of nylon 6 in the form of tire cords has been investigated by cyclic heating and cooling, using an environmental test chamber developed by Fabric Research Laboratories for the Instron Tester. A technique was developed enabling essentially continuous manual adjustment of load level while temperature was raised and lowered between limits encompassing passenger tire service conditions. The Instron was adjusted to cycle between minimum load limits of ±0.02 lb. at any selected level, so that response of the polyamide structure to rising or falling temperature was confined to length changes. Typical greige and commercially dipped-and-stretched 6 and 6,6 cords, tested in this manner, respond as shown in Figures 20 and 21.

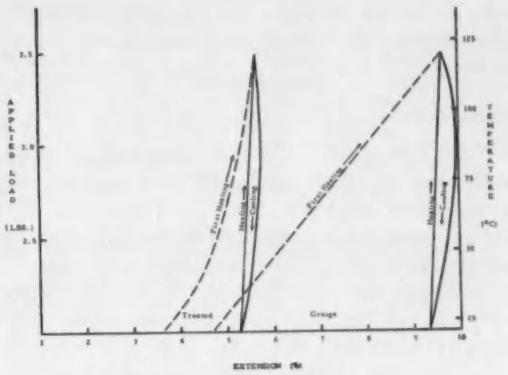

Fig. 20. HBT Caprolan tire cord.

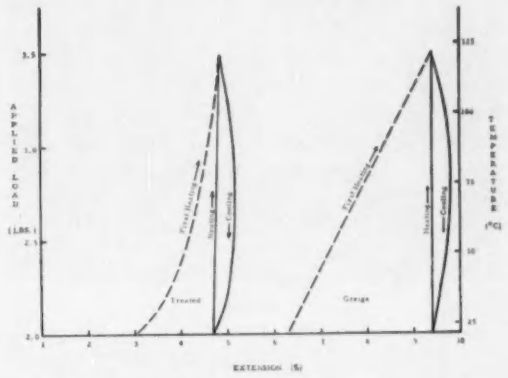

Fig. 21. Heat stabilized nylon 6,6 tire cord.

TABLE II. Elastic Recovery

	One cycle				Two cycles			
	Immediate elastic recovery		Permanent set		Immediate elastic recovery		Permanent set	
Elongation, %	6	6,6	6	6,6	6	6,6	6	6,6
5	1 : 1.00		1 : 1.03		1 : 0.99		1 : 1.52	
10	1 : 0.99		1 : 1.07		1 : 1.01		1 : 1.67	
15	1 : 0.98		1 : 1.11		1 : 1.01		1 : 1.72	
Loads, lb.								
5	1 : 1.03		1 : 1.04		1 : 0.91		1 : 1.52	
10	1 : 1.03		1 : 1.13		1 : 0.95		1 : 1.60	
15	1 : 1.00		1 : 1.14		1 : 0.96		1 : 1.57	

These results show that nylon 6 tire cords are

fully responsive to commercial tensilizing techniques, resulting in cords having good dimensional stability in service.

Retractive Forces

Since current tire cord processing technology involves heating of wet cord under tension (for drying of resin-latex dip) retractive forces have been studied, utilizing a boiling water bath especially designed for use with the Instron. A small yarn specimen is connected to a hook at the bottom of a vessel equipped with heating coils, then to another hook fixed to the Instron load-cell linkage, and a nominal load, sufficient to straighten but not stretch the specimen, is applied. Distilled water is added to the vessel until the specimen is completely immersed. The water is brought to the boil and held for 10 min. The heat is then cut off and the water drained, and the specimen is dried with a forced draft of air at room temperature. During the entire procedure, the specimen is held at fixed length, permitting direct recording of retractive forces on the load scale. Figure 22 shows the curves obtained in this manner for typical 6 and 6,6 tire yarns.

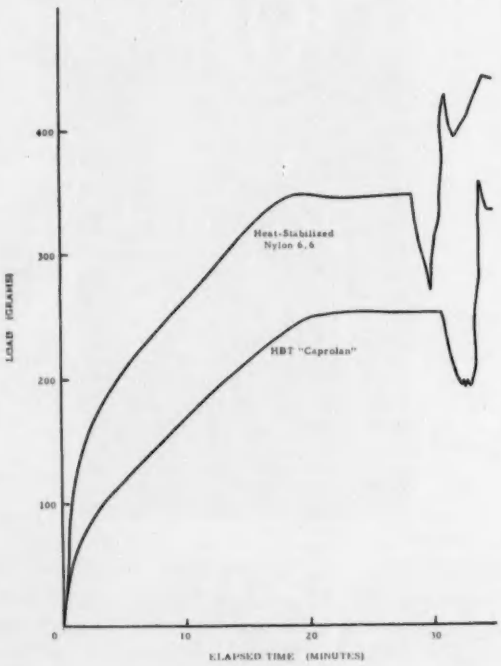

Fig. 22.

Two regions on the curve are used for calculations; one gives the tension level during the boil, the other being the highest point reached, which occurs during the drying phase. In the curves shown, HBT Caprolan gave values of 0.31 and 0.41 g./den., in comparison with 6,6 yarn values of 0.45 and 0.57 g./den., which are approximately 40% higher.

Tensilizing Response

Some aspects of fiber behavior are less predictable from the more commonly measured parameters—strength, modulus, etc. As might be surmised from the properties already described, nylon 6 is easier to process than nylon 6,6 in such operations as hot-stretching of tire cords.

Not only is less force required to impress a given degree of stretch upon HBT Caprolan cord at a given temperature, but the effective stretch obtained is higher with the 6 material. For example, in a series of tensilizing experiments conducted in a Litzler unit, at two stretch levels, the results listed in Table III were obtained.

Fatigue

The important attribute of fatigue resistance, especially critical in automobile tires, is prominently displayed in performance records established by HBT Caprolan. Our tire cord evaluation laboratory, utilizing the Goodrich disc compression tester, has conducted in-rubber fatigue tests on commercially treated cords from different sources, using two different types of stock. As is well known, in-rubber test reproducibility poses problems introduced by variability in rubber stocks and curing conditions. However, when both test and control specimens are cured together, and six of each are placed alternately in the discs, comparisons within a given test run may be considered valid. Typical test results, together with rotor and vibrator tests run in an outside laboratory, are shown in Table IV.

All of the equipment used in these tests is built by Ferry Machine Company from designs of the B. F. Goodrich Company. Use of the disc compression

TABLE III. Litzler Processing of Tire Cords

Impressed stretch, %	Cord tension, lb.		Effective stretch, %	
	Nylon 6	Nylon 6,6	Nylon 6	Nylon 6,6
14	6.1	7.8	12.4	8.7
11	6.0	8.0	10.4	6.4

TABLE IV. Laboratory Fatigue Tests

	Goodrich disc compression tester, percent cord strength retained				Goodrich rotor flex cord tester, hours to failure	Goodrich cord tension vibrator, hours to failure
Producer of cord	C	C	F	F	A	A
Rubber compound	G	R	G	R	none	none
HBT Caprolan	88.5	72.0	69.6	85.8	26.3	38.0
Heat-stabilized nylon 6, 6	83.3	47.5	57.7	84.2	10.5	22.5

tester in this type of work has been described by Swanson et al. [25]. In our work, a 12.5–6.3 compression–tension cycle was used, and specimens were flexed for 3,600,000 cycles before being dissected for tensile testing of the fatigued cords. The rotor flex tester is used primarily on greige cords and is so designed as to induce fiber-to-fiber friction within the cord with little external abrasion. This is a single cord test, run with a load of 5 lb. at room temperature. The vibrator subjects single cords to a load of 7 lb. in an oven held at 171° C. The load is caused to oscillate vertically at 60 cycles/sec. through an amplitude of 0.032 in. Both the rotor and vibrator tests are customarily run to failure.

Dyeability

The enhanced dyeability characteristics of nylon 6 fibers in general are now well established. Caprolan may be dyed successfully with the same types of dyes which are applicable to nylon 6,6. In addition, some selected dyes readily color Caprolan, yet show little or no affinity for nylon 6,6 fibers. The high saturation value of Caprolan permits the dyeing of certain deep shades which are difficult or unobtainable on nylon 6,6.

In general, Caprolan exhibits a higher strike than does nylon 6,6. For this reason, commercial dyeing procedures must be slightly different from those established for optimum processing of nylon 6,6. Necessary adjustments may be readily accomplished through time, temperature, and pH control or by the use of chemical retarding agents.

The difference in level of dye index between Caprolan and nylon 6,6 introduces to designers and stylists a vast potential in styling fabrics containing nylon which may be piece-dyed and yet exhibit tone-on-tone contrasts and cross-dye effects usually associated with yarn dyed fabrics.

Shrinkage Control

The first nylon textile yarns having controlled low shrinkage were developed and produced by Allied

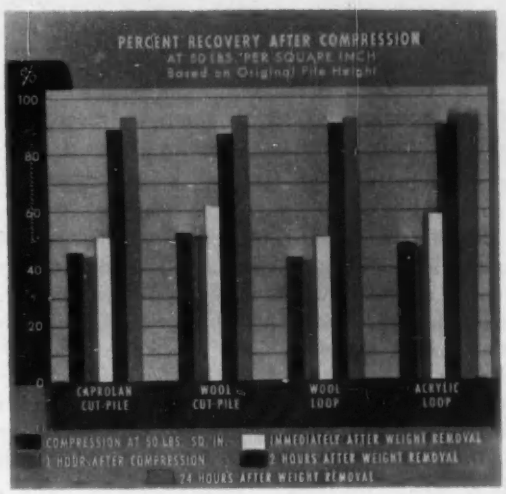

Fig. 23.

Chemical. Total boil shrinkage values of 7.5% have been achieved by means of radically new techniques in production. This type of yarn, produced without recourse to standard draw twister packaging, eliminates pirn-taper barré and obviates lag and inventory problems generally involved in conditioning conventional nylon yarns.

Heavy Denier Caprolan Yarns

Another area in which pioneering work has been done by our development group is in large package, heavy denier nylon yarns, for both industrial and textile uses. Produced in both 6 and 19 den./filament forms, these yarns combine high strength and durability with the excellent dyeing qualities of Caprolan and special adaptability to all of the conventional texturizing or bulking processes. A multiprocess heavy denier Caprolan yarn was the first to reach the commercial market in the floor-covering field.

Resiliency tests have shown cut-pile carpet made with this yarn to be fully as resilient as either cut

or looped wool and looped acrylic carpets of comparable construction. Measurements were made of pile height after varying recovery periods, following a 1-hr. application of 50 lb./sq. in. pressure, as shown in Figure 23.

Laboratory wear tests, using the Stoll flat-abrasion tester, showed marked superiority of the Caprolan carpet. Complete wear down to the backing required the following number of cycles: wool, 8250; acrylic, 17,158; Caprolan, 83,000. This is illustrated in Figure 24.

An idea of the extensive range of possibilities for obtaining various texturizing effects and degrees of bulking may be gained from Figures 25 and 26 [20].

Applications

Nylon 6, as a commercial fiber with widespread availability, is being successfully applied in many apparel and other textile uses, such as ladies' hose, tricot, fine dress goods; it is also used in blends with wool, cotton, and other fibers in suitings and work clothing and in knit goods, threads, upholstery, floor coverings, coated fabrics, and power-transmission components. Caprolan is well established in many of these fields, and is the leading nylon 6 fiber in tires, cordage, fire hose, webbings, upholstery fabrics, and texturized carpets.

Current Developments

Cordage Yarns

Studies of strength translational efficiencies in tire cords have shown HBT Caprolan to be outstanding in this property. This advantage is also realized when this yarn is used in cordage, particularly large marine hawsers. This has made possible the production of cordage which is stronger, weight-for-weight, than similar ropes made from 6,6 yarn actually having a higher original tenacity. Experimental overfinishes now under evaluation promise to add to this advantage a vastly improving service life, particularly in the wet repeat-loading, which is a large factor in towing operations. Fiber-to-fiber friction studies on 6 and 6,6 yarns, with and without overfinish, have been made using specially designed apparatus. Tests run under increasing loads serve to rate lubricity protection in terms of the maximum

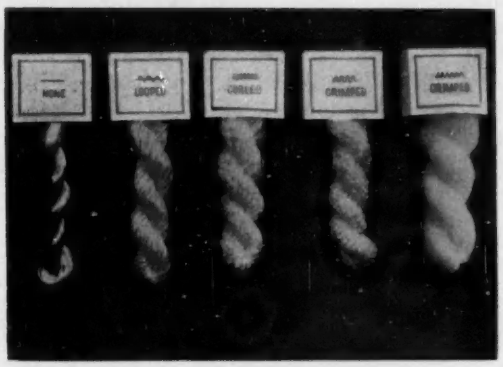

Fig. 25.

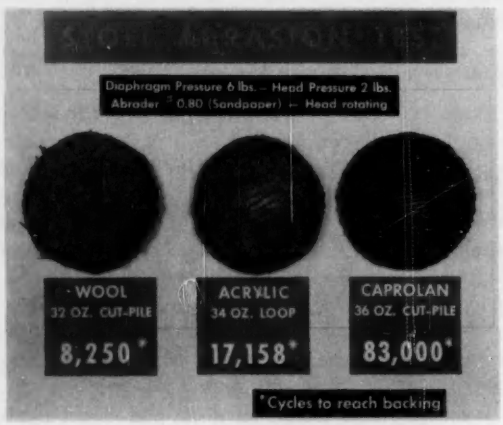

Fig. 24.

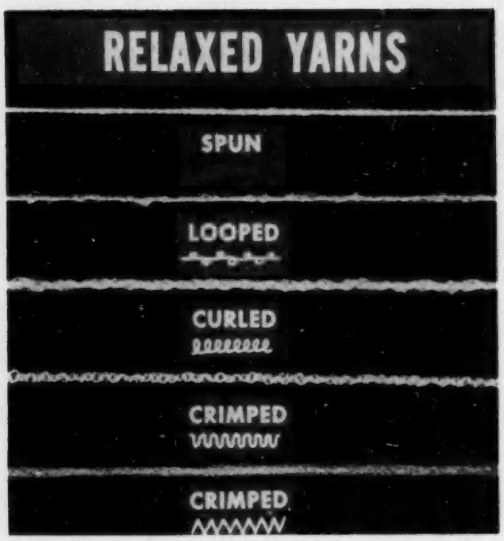

Fig. 26.

tension level reached before filament breakage commences. The beneficial effect of a proper overfinish in eliminating "stick-slip" frictional behavior is apparent in the oscillograph charts compared in Figure 27. In this work, the yarn speed was 1 cm./min. (2 cm./min. relative) with 500 g. pretensioning and 360° contact angle.

Degradation Resistance

In an approach to the problem of photodegradation of delustered nylon, studies on varied physical forms of delusterants have shown reduced degradation rates at concentrations equal to those used in 6,6 polyamides for producing semidull yarns. Other polymer systems still under development, containing newly developed heat- and light-stabilizing modifiers show durability superior to that of any known commercial polyamide yarn.

Yarn (840-den.) made from such a polymer, exposed to UV radiation in the 2537 Å band for 96 hr., retains 80% of its original tenacity, while heat stabilized nylon 6,6 retains 69%. In comparison with heat and light stabilized 6,6 polymer (210-den. yarns exposed for 200 hr. in a Weather-Ometer with 10 min. of water spray per hour), this experimental polymer retains 93% of its original tenacity against 87% for the 6,6 type.

Copolymers

Thus far, most of our work in the field of nylon 6 has been basically centered on polycaprolactam itself. Initial efforts were directed toward not only producing a good general textile yarn from nylon 6 but also in engineering this yarn for adaptability to texturizing processes and in developing good industrial type yarns. Current work consists not only in studying physical modifications of Caprolan which will assist in achieving successful end-use performance, but in experimentation on chemical modifications of nylon 6; for example, copolymers of caprolactam and other functional compounds. Potential improvements in fiber properties are indicated by these studies. Fibers made from such experimental copolymers show significant gains in tensile properties, ability to withstand exposure to elevated temperatures, and increased melting point over conventional polycaprolactam fibers.

Further Potential

The relative economy and simplicity of production of 6 polymer from caprolactam give promise of still further development. Polymerization is carried out at low pressures, and relatively small quantities of water have to be withdrawn from the polymerization site. Continuous polymerization, a key to better

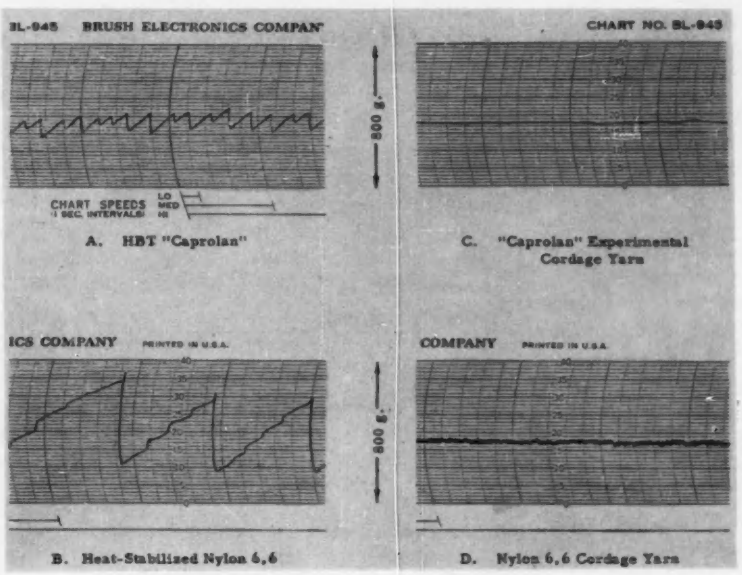

Fig. 27. Yarn-to-yarn friction.

uniformity, higher quality and still lower costs, is more feasible than with nylon 6,6.

Summary

Nylon 6 has been shown to be quite similar to nylon 6,6 in many important areas. Even at the molecular level, structural similarities are striking, and a satisfactory explanation of the melting point difference has been proposed. Response of undrawn 6 polyamide to drawing agrees with predictable data based on experience with 6,6. Refinements in fiber production technology are building up experience with steadily increasing tenacities and decreasing shrinkages, which parallel the history of nylon 6,6. Dissatisfaction with early Perlon yarns has been largely overcome by the improved properties of modern nylon 6. These experiences confirm the fact that Carothers' statement ". . . the properties of a very high molecular material may vary over a wide range, depending upon the physical treatment it has received" [3] applies with equal force to the 6 and 6,6 polyamides. The lesson has not been lost on the producers of the newer type. Already, nylon 6 has successfully demonstrated advantages in dyeability, elastic recovery, fatigue resistance, retractive force levels, and thermal stability, among aspects of major importance in engineering and consumer applications of textile fibers.

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Advancing Frontiers of Nylon and Dacron[1] Polyester Fibers[2]

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Abstract

Several examples of what is believed to be typical of the principal direction of evolution of thermoplastic fibers are given—i.e., the development of special nylon and polyester fibers that, while retaining their basic fiber qualities, will be tailored for specific end-use applications. The preparation of these special fibers has been accomplished by making use of the thermoplastic nature of nylon and polyesters. By changing the manufacturing process, a nylon staple fiber has been developed that has a load–elongation curve similar to that of cotton; blends with cotton containing only 25% of this nylon showed an average improvement in fabric life of 70% over that of cotton alone. Another modification of nylon is designed specifically to give carpets a luxurious hand with soil and crush resistance, intrinsic durability, and freedom from fuzzing or pilling; this specially engineered fiber has a selected denier, roughly triangular cross section, and a curvilinear crimp. The use of a sewing thread of Dacron specially prepared so that it will elongate when ironed has greatly alleviated the problem of seam pucker in garments. Finally, a lightweight nylon tricot fabric with excellent covering power and handle can be obtained by Schreiner calendering 20-den. nylon tricot fabric and then finishing it by beck-working.

Introduction

During the 20-year history of nylon, and even since the Du Pont Company first made Dacron polyester fiber available on an experimental basis in 1950, substantial advances have been made in the science and technology of melt-spun fibers and their textiles. These advances have resulted in a volume of scientific and patent literature of enormous size. Yet we know that all areas of study in this field, from the chemistry of polymers to textile processing, will engage the attention of scientists and engineers for many years to come, because the experts, in their individual fields, confess to have hardly scratched the surface. However, the scientific and technical cornerstones of synthetic melt-spun fibers have been firmly laid, and it is the purpose of this paper to analyze what we believe is the principal direction of growth for these fibers in the future.

We believe that in this next phase of development, new nylon and Dacron yarns will be developed that, while retaining their basic fiber qualities, will be tailored for specific end-use applications. Furthermore, by the use of principles now in hand, the physical properties and geometry of nylon and Dacron will be modified in fiber form, in yarn form, in fabric, and in the end-use article, to arrive at an ever-increasing variety of optimum textile structures.

Chemical Modifications

Of the almost infinite variety of textile structures that can be obtained by chemical modification of a basic polymer, we shall mention but one that has great commercial significance—Dacron Type 64 polyester fiber. This new fiber was engineered primarily for suiting fabrics in blends with wool. It has the same basic properties of all Dacron polyester fibers, but has built into it other features that now make possible the construction of a much wider variety of suiting fabrics of excellent aesthetics and resistance to pilling than was available from Dacron Type 54 staple.

Working with this new fiber, a number of mills have produced fabrics, from blended worsted-spun yarns, that have much greater cover and cover stability than those from Type 54. We have also made soft, woolen-spun fabrics from blends of wool with Dacron Type 64 that are completely satisfactory in performance. We believe this new fiber, created for

[1] Du Pont trademark.

[2] Presented at the Annual Meeting of the Textile Research Institute in New York City on March 24, 1959.

a special end use, is an important advance in broadening the versatility of Dacron. Its new properties depend on a chemical change in the fiber, and not on any modification of its thermoplastic properties.

Modifications Dependent on Thermoplastic Properties

Physical changes in the fiber can also be used in the development of new products for specific end uses. One key to the variety of products that we anticipate, over the coming years, is the thermoplastic character of nylon and Dacron. In its simplest and best known application, this property can be used to put an ironed crease into fabrics of these fibers that will not be removed by water and will come out only if ironed flat again at a temperature somewhat higher than that at which it was put in.

An examination of the classical picture of polymer fine structure will show how this thermoplastic nature can be used to engineer specialty fibers. As is well known, polymer structure in synthetic fibers is pictured as being made up of two different types of molecular assemblies. One is the crystalline portion—with a structure as well defined as any other organic crystal, like sugar. The second is the amorphous portion, consisting of less-ordered polymer chains. This amorphous portion provides the spring-like character to the fibers, i.e., their resilience and longer term recovery from deformation. As the temperature of this structure is raised, for example by ironing at 230° F., a complex set of interactions occurs between these two polymer arrangements: the crystalline portions, which have a melting point higher than the ironing temperature, are relatively unaffected, the major result being a softening of the amorphous portions, which now, under imposed stress from the iron, take on their most comfortable positions at this temperature. The molecules form new bonds with their neighbors, either in the crystalline or the amorphous phase. If the structure now is quickly cooled, those new bonds are frozen in place, and any physical deformation such as a crease, that is formed at high temperature, is correspondingly frozen in place. To remove this crease it is necessary to remelt the bonds formed in ironing. In other words, the fabric has a "memory" for the temperature at which the crease was formed.

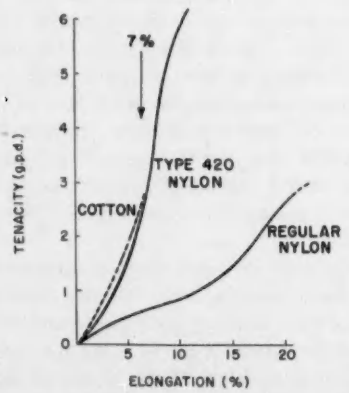

Fig. 1. Stress–strain curves of regular and Du Pont 420 nylon compared with that of cotton.

Put to work either by fiber maker or fiber processor, this property of form setting with heat is what we believe to be an important key to the continuing evolution of nylon and Dacron toward maximum usefulness in textiles.

Nylon for Blending with Cotton

It is obvious that one should be able to improve the strength and abrasion resistance of cotton fabrics by blending into the cotton yarns a small amount of nylon. First experiments, however, revealed that, however obvious the conclusion, the strength of the fabrics from blended yarns was actually decreased. Flex abrasion was markedly improved, as expected.

In retrospect, one could hardly expect any other result, since the stress–strain curves of the two fibers shown in Figure 1 were such that at the breaking elongation of the cotton fiber at 7%, the nylon was contributing only about 0.5 g./den. to the strength of the structure. Although the problem was partially spelled out by Dennison and Leach [1], the solution was not immediately obvious. After several false starts, work was undertaken to develop a nylon staple fiber with a load–elongation curve to match that of cotton, with the specific target of equalizing the properties of cotton at 7% elongation. By changing the manufacturing process to adjust the spring-like amorphous portions and to anchor this new molecular configuration to retain these properties at temperatures higher than the blend fabric would encounter in its use, a permanently fixed stress–strain curve was built into the new fiber, called Du Pont 420 nylon, that allows it now to contribute not only to the improvement in abrasion, but to the strength of the fabric as well. The stress–

TABLE I. Effect of Nylon Reinforcement on Properties of Twill Fabrics

Fabric composition	Flex, abrasions	Breaking strength, lb.	Tearing strength, lb.
Cotton	1378	191	9.0
Cotton + regular nylon (25% nylon in warp)	6750	171	8.7
Cotton + duPont 420 nylon (25% nylon in warp)	6750	242	11.4

strain curve of the new fiber is also shown in Figure 1.

Translated into end-use terms, the use of a warp consisting of 75% cotton–25% Du Pont 420 nylon resulted in an average improvement in fabric life of 70%. Figure 2 shows comparative photos of twill work pants taken after 30 and 38 wearings by one of the wear-testers. Quantitative data showing the effect of nylon reinforcement on the properties of twill fabrics are given in Table I.

Despite the simplicity of this example, it contains the elements that can be used as guides for the development of many other specialized fibers: definition of an end use to which the fundamental properties of nylon and Dacron can make a contribution, basic work to analyze the special properties that the fiber must have to make the optimum contribution, and scientific and engineering knowledge to achieve these properties in an economical fashion.

Nylon Engineered for Use in Carpets

Viewed broadly, the basic characteristics of nylon are those that are needed in carpets: durability, deriving from nylon's strength, toughness, and abrasion resistance; its ability to recover from high deformations; and soil resistance and washability, related to its hydrophobic character. All of these properties have been effectively put to work in carpets of 100% nylon staple and of wool–nylon staple blends.

A limitation of this development has been the number of styles into which nylon can go, due to the formation of fiber pills and fuzzing of the carpet surface. For example, an improperly constructed nylon staple carpet after 2 years of wear is shown in Figure 3. The appearance is the result in part of the toughness of the fibers, because the pills are held to the carpet surface by fibers that are not easily broken. Although this problem can be quite

Fig. 2. Wear performance of twill work pants.

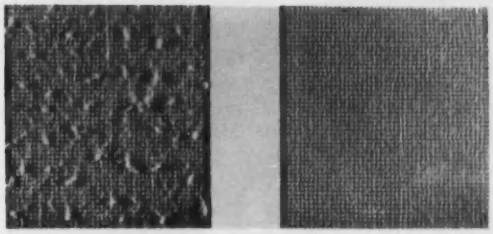

Fig. 3. Pilling of nylon staple carpets (wear equivalent to two years of home service).

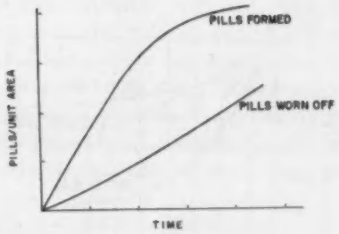

Fig. 4. Rate of pill formation and removal.

satisfactorily controlled by known methods in many carpet styles, it has not been possible to use nylon staple in loop-pile carpeting made from the woolen-spun yarns used by most carpet-makers.

On analysis, it is clear that the carpet-maker must face two well-identified processes in the life of a carpet. The first of these is the rate at which pills form, shown schematically by the upper line in Figure 4, and their disappearance, or wear-off, in the lower line. The arithmetical difference between these curves is the number of pills that can be seen on a carpet at any time after it is put in use, and is one measure of its acceptability.

Thus, from this figure, it can be seen that one way to minimize pill concentration on the carpet surface is to increase the rate of wear-off, closing

the gap between the curves. However, this method must result in a higher rate of fiber loss from the carpet, and consequently could lead to appreciable loss in durability if carried too far. With the reserve of toughness available in nylon and Dacron, relative to wool, it is possible to make a satisfactory compromise between durability and pilling. This has been done in the case of Dacron Type 64 polyester fiber, mentioned earlier, which shows complete surface stability in a wider range of fabrics than was available from Dacron Type 54, but still has greater fiber flex resistance, and loop toughness, than wool. But the best way to solve the problem in carpets, where we want permanent durability, is to reduce the rate of formation of pills to zero, which can be done by using a continuous filament yarn instead of a spun staple yarn.

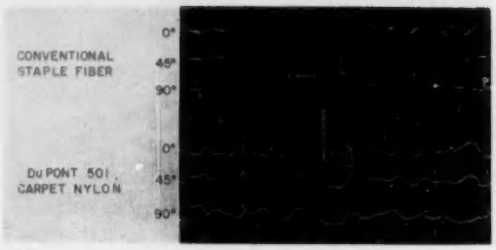

Fig. 5. Crimp of carpet fibers.

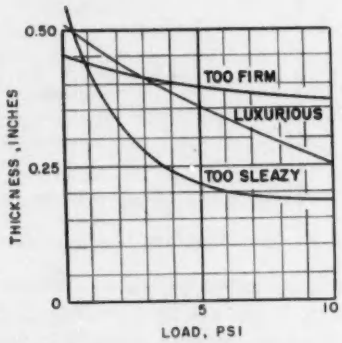

Fig. 6. Carpet compression curves.

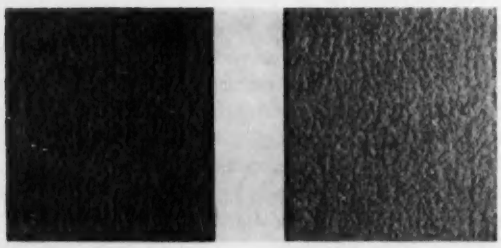

Fig. 7. Floor soiling tests on nylon carpets. Left, round cross section nylon carpet staple; right, 501 carpet nylon.

At this point, we have carpeting defined as an end use which capitalizes on the fundamental properties of nylon, and the method (that is, the use of filament yarn) by which a pilling problem can be avoided. The next step in the development was to build into the fiber the special properties that fit it specifically for optimum utility.

First, bulk was achieved by the development of a fiber with curvilinear crimp in three dimensions that makes Du Pont 501 carpet nylon a more effective space filler than a fiber whose crimp is two-dimensional. What is needed for maximum initial bulk is maximum interference, in three dimensions, between fibers. For bulk retention we must design fibers that are geometrically incapable of getting any closer together as they move about in use. From Figure 5 one can see that the fibers with curvilinear crimp cannot fit together as conveniently as can those with two-dimensional crimp.

Bulk, and bulk retention, do not comprise all of the mechanical properties we look for in the face of the carpet. We need also to adjust compressional characteristics, or load supporting power. We have

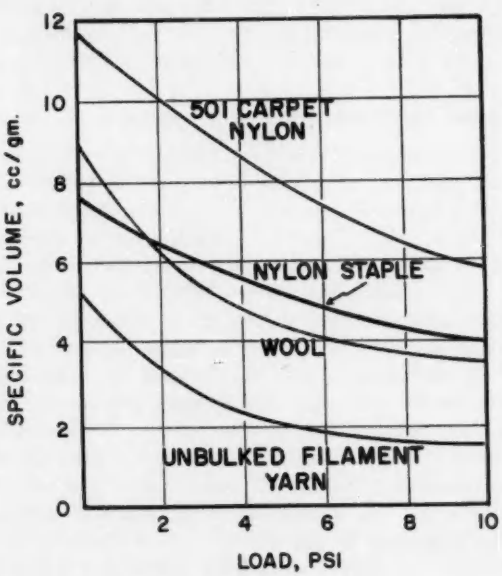

Fig. 8. Yarn bulk in carpets.

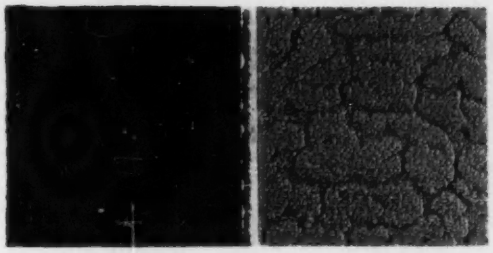

Fig. 9. Carpets of Du Pont 501 carpet nylon. Left, woven "Artisan" by James Lees & Sons Co; right, tufted "Vega" by E. T. Barwick Mills.

been able, with different structures, to achieve thickness vs. load curves for carpeting of a wide variety (see Figure 6). To get the right compressional properties, one adjusts the fiber stiffness and the number of supporting fibers per unit area.

Fiber stiffness is a function, of course, of denier. Stiffness is also dependent on cross section. Too highly modified cross sections, such as thin ribbons, collapse under heavy loading. We have found that a tri-lobal filament, i.e., one with roughly triangular cross section, with a stiffness of 1.6 relative to the stiffness of 1.0 for a round filament, is the best for our purpose. With this cross section, optimum filament denier is 18.

A second benefit of this cross section is its improvement in discoloration due to soiling. The triangular fiber is less transparent, with the result that it retains its appearance better than a round fiber, apparently because one cannot see the dirt on more than one side of the fiber. We have had difficulty developing instrumental methods to measure this improvement, but subjectively the point is easy to establish. Figure 7, showing two carpet samples wear tested under carefully controlled conditions for 32,000 cycles, tells the story quite well.

We now have the following elements engineered into the carpet fiber: the curvilinear crimp, selected denier, and cross section for stiffness and retention of clean appearance. The benefit of using such a fiber in a carpet face is shown in Figure 8, which relates the specific volume of the fiber in the carpet face to applied pressure in pounds per square inch. For most purposes, a reading at .3 lb./sq. in. characterizes the fabric handle and load supporting power. Of course, as a result of the better bulk and load supporting power, the amount of fiber in the carpet can be substantially reduced to make it equivalent in compressional characteristics to carpets of other fibers, or more luxurious carpets can be achieved with greater amounts of fiber. The actual reduction in weight depends, obviously, on carpet construction, yarn twist, and other factors.

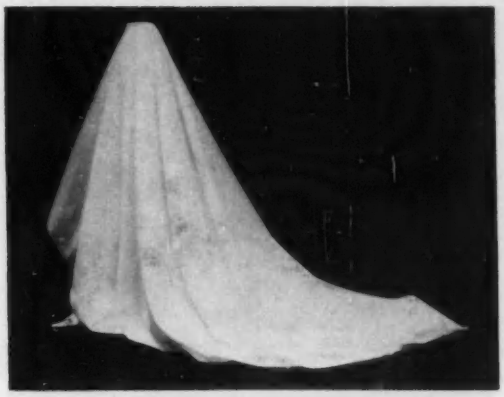

Fig. 10. Shirting fabric—65% Dacron and 35% rayon.

The total result, then, of the development of Du Pont 501 carpet nylon is a fiber with the intrinsic durability and crush resistance of nylon that suit it to carpeting, together with the special properties that give us carpets of all styles that will not pill or fuzz, have a luxurious hand, are resistant to soiling, and cost no more than other carpets in the market today. Figure 9 shows two carpets made of Du Pont 501 carpet nylon by E. T. Barwick and James Lees & Sons, who cooperated with us in this development.

Elongating Sewing Thread

Figure 10 shows the appearance of a shirting fabric made from a blend of 65% Dacron and 35% rayon after a standard automatic washing and tumble drying in commercially made home equipment. This level of performance, which we think is quite good, certainly does not prepare us for the appearance of the garment in Figure 11, which is obviously disappointing. The difference between fabric and garment, on closer inspection, is found to be due only to puckering of the seams, the fabric performance being the same in the two cases.

Careful analysis has shown that all three of the elements in sewing—the sewing machine, the fabric, and the thread—can contribute to poor seam formation. Seam puckering caused by the sewing machine can be eliminated by its proper adjustment, according to a procedure discussed by Hardy [2].

Fig. 11. Shirt of 65% Dacron–35% rayon fabric demonstrating poor seaming technology.

The fabric, in addition, must be stable in use, or sewing technology of any kind won't help it.

But if the right machine adjustment is made, and stable fabrics are sewn, the seams of wash and wear garments are still not perfect because the fabric is gathered within the loop formed by the top and bottom thread (Figure 12). This gathering, which results from the temporary elongation of the sewing thread under the stresses of stitch formation at high speed, could be eliminated by the use of a thread that could grow in length after the stitch was formed.

Surprisingly, a fiber like this, to make an elongating thread, had been turned up in exploratory work in our Dacron Research Laboratory. This unusual property depends on first creating in the manufacturing process a special molecular structure in the yarn, which it retains through conversion to thread and sewing, and then converting this to a second molecular structure by heating the thread—that is, ironing it.

The molecular processes involved seem to be related to the conversion of amorphous polymer to crystalline polymer. In Dacron, we believe what happens is this: under the right conditions a fiber can be formed with a molecular structure that is oriented to some extent but has virtually no crystalline component. The schematic diagram of this structure is shown on the left in Figure 13. This amorphous structure is thermodynamically unstable, but cannot crystallize because its very high internal viscosity won't permit the molecular segments to flow into their preferred structure. It is really a supercooled liquid.

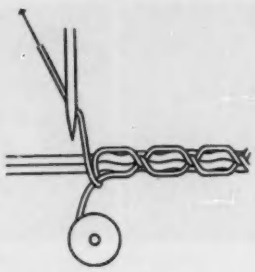

Fig. 12. Fabric "gathered" by tension of sewing thread.

However, when this fiber is heated, the internal viscosity drops and the intermolecular attractive forces are sufficient now to move the segments, with the result that crystallization occurs, as shown on the right in Figure 13. This in turn brings about a molecular straightening, in the axial direction, which causes the fiber to lengthen. One can get various degrees of elongation, depending on the structure that is built into the fiber, but 15% length increase turned out to be right for sewing thread.

In practice, it has been established that both the upper and lower threads should not be elongatable. The upper thread should preferably be made of a high modulus Dacron yarn with high strength to withstand the tensile stress and abrasion of the needle action, and only the bottom thread need elongate to restore the fabric to a flat unpuckered state.

The result of this technology on fabric seam improvement can be measured with a simple device, called of course a "puckerometer," that determines the length that a seam must be extended to make it flat. Using this instrument, shown in Figure 14, we obtained the data in Table II that clearly indicate how much of an improvement can be achieved. The same results, in subjective terms, can be seen

TABLE II. Improvement in Seam Puckering (Taffeta Fabric)

	% Pucker		
	As sewn	After pressing	After 5 "C" washes
Top and bottom threads of Dacron	1.7	1.4	2.3
Top thread, Dacron; bottom thread, exp. Dacron	1.0	0.0	0.6

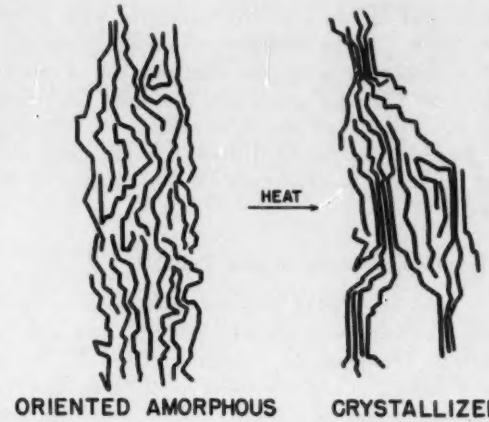

Fig. 13. Molecular arrangement in synthetic polymer fiber.

in the comparison of two shirts of Dacron and rayon blend fabric shown in Figure 15, the one on the right showing the result of the combination of optimum machine adjustment, stable fabric, and elongatable sewing thread.

We are now attempting to find out in scaled-up experiments how practical this development is going to be. Whatever the result, this development does provide an excellent example of the versatility of Dacron and the adaptation of one basic fiber to meet specific end-use requirements through proper modification.

Bulked and Stretch Yarns

These examples of fiber engineering—a nylon for blending with cotton, a filament carpet yarn, and a sewing thread of Dacron—are possible only by substantial changes in manufacturing conditions, and are impossible or very uneconomical to achieve in a textile mill. However, over the past several years, a number of significant developments have been made by throwsters, in which the character of filament yarn has been greatly modified and improved for specific end uses by processes that depend on the thermal properties of nylon and Dacron. The conversion of standard filament yarns to "stretch yarns" that have found such a solid market in hose, and have more recently been expanding into other apparel, is an outstanding example.

TABLE III. Properties of Fabric From Saaba * Textured Dacron Yarn

	Dacron	Saaba Dacron
Weight, oz./yd.²	2.05	1.76
Bulk, cc./g.	1.46	2.51
Covering power, %	74.1	85.6
Air permeability	65.7	75.6
Fabric/fabric coefficient of friction	0.48	0.79

* Trademark of Universal Winding Co.

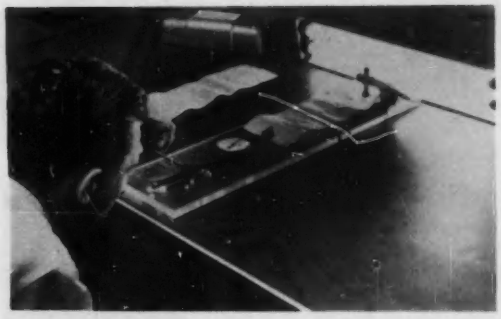

Fig. 14. The puckerometer.

Fig. 15. Seaming technology in shirts.

Figure 16 is a photomicrograph of "Superloft" stretch nylon, together with the starting yarn, that speaks volumes for the permanent reformation that has been achieved.

A second type of fiber modification carried out by our customers is exemplified by several bulking processes, applicable both to nylon and Dacron. All of these depend on holding the fiber in a crimped or strained condition while being heated. The new crimped configuration is set in the yarn at a temperature higher than it will encounter in its use. Figure 17 shows "Ban-Lon" bulk nylon, along with the starting yarn.

It is difficult to express in numbers all of the

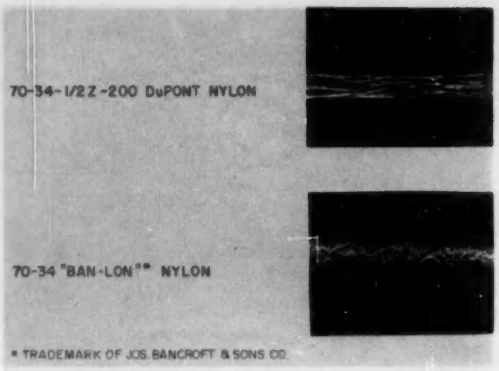

Fig. 16. Stretch yarn (Superloft).

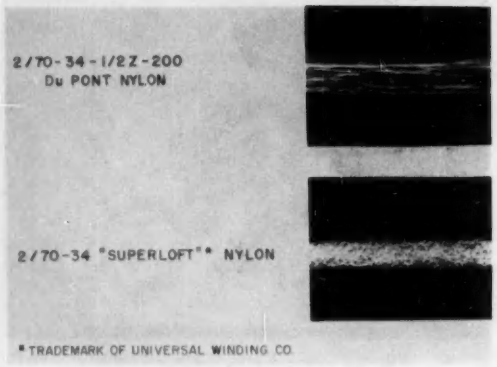

Fig. 17. Bulk yarn (Ban-Lon).

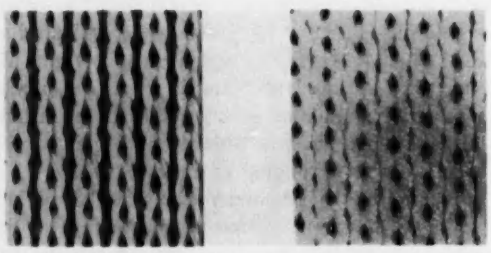

Fig. 18. Effect of Schreiner-calendering on 20-den. nylon tricot fabric. Left, before; right, after.

changes in fabric aesthetics and performance that are achieved by these bulking processes, but the data in Table III reflect some of the effects on bulk, cover, and friction that are produced in a woven fabric made from a bulked yarn.

Modification of Fabric Properties

So far, we have discussed examples of fiber modification, through utilization of thermoplastic properties, that can be achieved before the yarn is put into fabric. As we consider next the modification of fabric properties by thermal treatment we, of course, encounter finishing procedures that have been used as long as nylon has been in existence. Preboarding, or shape-setting, has been the key to the permanent and attractive fit of women's nylon hosiery for 20 years.

Schreiner-Calendered Nylon Tricot

A good example of a fabric engineered for optimum acceptability in a specific end use, by a specific finishing procedure, is Schreiner-calendered nylon tricot fabric. Certainly there is nothing new in Schreiner-calendering itself—it has been used for many years on fabrics of all types. It consists of passing the fabric under pressure between heated rolls that have a finely embossed surface.

Actually, our starting point in this development was based on some long-term studies on apparel comfort, one part of which was devoted to the comfort of lingerie fabrics. The tests were run in sufficient depth to obtain statistically sound data. Slips were evaluated by a panel of 20 wearers, in controlled conditions of humidity and temperature, and in semidarkness, wearing gloves, to avoid bias from appearance and handle. From these studies we formed several conclusions that make up the basis for end use research still underway, but one conclusion was that reduced fabric weight was of major importance in improving comfort.

With the merit of reduced fabric weight clearly defined, together with the necessity of retaining fabric opacity, we started detailed work on Schreiner-calendering. First results of our work on 40-den. nylon tricot were published by Richardson [4]. Our research was continued, however, because our interest lay in lighter weight fabrics, made of 20-den. yarns. Figure 18 is a picture of a 20-den. fabric that shows the extent of fabric deformation produced by calendering, photographed against a dark background to reveal the improvement in cover.

However, Schreiner-calendering of 20-den. tricot fabrics gave disappointing results at first, because interfilament mobility was crushed out of the fabric, and a papery handle and poor wrinkle recovery were obtained. More work on finishing procedures showed that warm–wet mechanical action on the fabric, such as achieved in a beck, would relax the

fabric sufficiently to restore interfilament mobility. There is scarcely any difference in other properties brought about by beck-working. The net result of this development was a fabric with the handle, appearance, and performance that we were looking for, together with a marked reduction in fabric weight. A comparison of the new fabric with conventional 40-den. tricot fabric is made in Table IV.

TABLE IV. Comparison of Nylon Tricot Fabrics

	20-Den. Schreiner calendered	40-Den. not calendered
Weight, oz./yd.²	1.86	2.68
Thickness, mils	6.5	10.5
Covering power, %	11.9	14.0

Fabric Finishing

The fact that a warm–wet treatment in a beck restores a pleasing handle and wrinkle recovery to the fabric, without having visibly changed its structure, is a good example of the subtle changes in fabric geometry that can be brought about in finishing. We are making some progress in the analysis of these factors: as an example, let's consider the problem of achieving maximum resilience in a fabric of nylon.

First, of course, we have the intrinsic spring-like character of the fine structure that stores the energy of deformation and returns the fiber to its original configuration. Without restraint, this recovery is remarkably complete, but how well this recovery process can work in the fabric depends on the forces that the fiber must overcome. These forces are mainly frictional and thus are determined by how readily the fibers slide past one another, which depends in turn on the tightness of the fabric structure and the characteristics of fiber surface. All these elements of form recovery are easily recognized in the behavior of a loosely knitted structure.

This concept of fiber mobility has been well recognized by finishers who are building better properties into fabrics of nylon through relaxed heat setting, and into fabrics of Dacron through procedures (involving calendering, heat-setting, and treatment with caustic) that permit easier interfilament action. The use of this concept will permit us, over the coming years, to establish optimum fabric geometry by learning how to use heat more effectively, just as water is used today to establish the geometry of fabrics of natural fibers.

Advantages to the Consumer

Thus far, we have shown how the thermoplastic character of fibers has permitted the *development* of new fibers, yarns, and fabrics that are making better end-use articles available to the consumer. In the hands of the consumer, as he uses these articles, the thermoplastic character of the fibers continues to be of great importance, because it is responsible for the *retention* of the end-use properties that he buys.

Creases and pleats that stay in, fabrics that resist mussing and wear wrinkling, and hosiery that doesn't sag are some of the benefits to the consumer of the permanent thermal memory of these fibers. Beyond these advantages lies the entire field of wash and wear performance of garments of Dacron and its blends. The principles of wash and wear performance have been given by Peterson [3]; it is therefore appropriate here only to point out that these principles also depend on the same basic fiber chemistry and physics that are discussed above. As important and exciting as all of us recognize wash and wear performance to be, from a purely technical viewpoint it is just one part of a much broader opportunity to utilize the thermal properties of nylon and Dacron.

Conclusion

We have attempted to show here that nylon and Dacron fibers are basic structural materials with a versatility that we are only starting to appreciate. We believe that these fibers, like other basic structural materials in the past, are entering a second phase of their evolution, in which optimum forms of these fibers, and their fabrics, will be developed for specialized end uses. Because it is an older fiber, nylon has evolved farther into this second phase than has Dacron. Although this discussion has been essentially limited to the variety of end-use products made possible by their thermoplastic nature, we should remember that there are other degrees of freedom available in nylon and Dacron that are leading to important advances in textile technology. Fortunately, this evolution, already underway, is not going to depend on the imagination or technical resources of any one group, but will, rather, present an

opportunity for new developments in all phases of textile manufacturing.

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An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer

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Abstract

An empirical method for determining the crystallinity of native cellulose was studied with an x-ray diffractometer using the focusing and transmission techniques. The influence of fluctuations in the primary radiation and in the counting and recording processes have been determined. The intensity of the 002 interference and the amorphous scatter at $2\theta = 18°$ was measured. The percent crystalline material in the total cellulose was expressed by an x-ray "crystallinity index." This was done for cotton cellulose decrystallized with aqueous solutions containing from 70% to nominally 100% ethylamine. The x-ray "crystallinity index" was correlated with acid hydrolysis crystallinity, moisture regain, density, leveling-off degree of polymerization values, and infrared absorbance values for each sample. The results indicate that the crystallinity index is a time-saving empirical measure of relative crystallinity. The precision of the crystallinity index in terms of the several crystallinity criteria is given. Based on over 40 samples for which acid hydrolysis crystallinity values were available, the standard error was 6.5%.

THE importance of the degree of crystallinity of cellulose to an understanding of the behavior of cellulosic materials has led to considerable interest in the development of a rapid and reliable quantitative method for its determination. Ward [23], in a review of the fine structure of cellulose, discussed the most frequently used methods for determination of the degree of crystallinity in cellulose and also the measurement of other closely related parameters. Nichols' [15] review of the subject covered the x-ray as well as infrared techniques developed for cellulose and other high polymers.

It is apparent in these reviews that the x-ray method proposed by Hermans and Weidinger [4] has obtained considerable acceptance. In their method, rigid controls of sample and instrumental variables are necessary, and photographic recording of the diffracted beam is employed. The integrated intensity of the radial interferences obtained by tedious photometering of the photographic plates is used as a measure of the proportion of crystalline material present. To represent the proportion of amorphous cellulose present, Hermans and Weidinger adapted the findings of Hess and coworkers [5] to their data. The latter workers found that prolonged grinding of crystalline cellulose in a ball mill resulted in the almost complete disappearance of the characteristic x-ray interferences. The broad diffuse halo with a maximum intensity at an inter-

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planar spacing corresponding to 4.8 Å was assumed to be indicative of amorphous scattering. Hermans and Weidinger, using corrected data taken from the photometer charts, computed absolute values for the percent crystallinity of the materials they studied. Their procedure is based upon the hypothesis that the diffractions from crystalline and amorphous materials are additive. Meyer [12], however, finds such a procedure doubtful and questions the significance of the percentages obtained in this manner.

More recently, Wakelin, Virgin, and Crystal [22] have developed a high precision x-ray diffractometric technique for the determination of the degree of crystallinity in native cellulose. However, this technique and that of Hermans and Weidinger have limited applicability for routine operations because of the time required for their use.

Ellefsen, Lund, Tonnesen, and Oien [3] made an extensive study of the nature of amorphous cellulose and developed a diffractometric method for the determination of a "degree of amorphity" of cellulose. These authors disagree with Hermans and Weidinger [4] on the general intensity distribution of the scattering contribution from amorphous cellulose. In the work of Ellefson and coworkers, however, the significance of the values obtained for the "degree of amorphity" is limited by lack of comparison with results obtained using other accepted methods for the determination of crystallinity in cellulose.

Segal and coworkers [11, 20] have indicated that cotton can be greatly reduced in crystallinity by treatment with ethylamine. In connection with this work, a routine method for the estimation of the degree of crystallinity of native cellulose in cotton has been developed. This paper describes the application of the x-ray diffractometer to the problem and the correlation of the x-ray values with values obtained by other generally accepted physical and chemical methods for evaluating the degree of crystallinity of cotton.

Experimental Methods

Studies on the Instrument

An early model Norelco[3] 90-degree x-ray diffractometer modified by the addition of Soller slits [21] was employed for obtaining the diffraction tracings. In the instrument the specimen is mounted vertically while the Geiger counter moves on a horizontal quadrant. The collimated beam was filtered with nickel foil to remove K-beta radiation. The primary beam was defined at the x-ray port by a slit opening 1.2×11 mm. The diffracted radiation entering the Geiger counter tube was further defined by two slit openings. The first, immediately in front of the tube, had dimensions of 0.2×11 mm.; the second, 42 mm. farther out in front of the first slit, measured 0.7×11 mm.

The x-ray generator was operated from a constant-voltage transformer, and current regulation was applied in the cathode circuit of the x-ray tube. The Geiger counter and scaling circuit power supplies, as well as the recorder, were operated from a separate constant-voltage transformer. The equipment was energized continuously, except for the high voltage which was turned on at least 30 min. prior to use. Prior to each recording, the performance of the instrument was checked by obtaining from a brass standard plate a tracing of the diffraction peak at $2\theta = 42.2°$. Necessary adjustments were made to maintain an arbitrary fixed level of recording.

The stability of the x-ray beam, or the absence of drift in its energy content, was determined in the following manner. A continuous recording was made over a period of 15 min. of the diffraction from a brass standard plate with the Geiger counter fixed at $2\theta = 42.2°$. The high and low levels of the recorded intensities were measured at 0.5-min. intervals and the data analyzed statistically. With the x-ray generator turned off, a source of gamma radiation subject only to statistical fluctuations in intensity [10] was positioned to give a recorded intensity of radiation approximately the same as that from the x-ray generator. A tracing was obtained then from the gamma source, and the same statistical analysis was made of the data. A record of the counting rates was also obtained during these operations, this being done at the same time as the recordings were made. Comparison of the data from the x-ray generator with those from the gamma source is shown in Table I.

The absence of drift in the energy of the primary x-ray beam is indicated by the data given in Table I. The close agreement between the x-ray data and the gamma radiation data shows that the use of constant voltage transformers and continuous excitation of the electronic components of the instru-

[3] It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

TABLE I. Comparison of Radiation from X-ray Generator with That from a Radioactive Source, Geiger Counter Stationary*

Method of recording	Source of radiation	Mean intensity, arbitrary units	Mean counts per sec.	Standard deviation	Coefficient of variation, %
Strip chart recorder	X-rays diffracted from brass at $2\theta = 42.2°$	7.41	—	±0.11	1.5
	Gamma radiation from radioactive source	7.29	—	±0.12	1.7
Mechanical register	X-rays diffracted from brass at $2\theta = 42.2°$	—	237	±1.5	0.62
	Gamma radiation from radioactive source	—	232	±1.5	0.63

* All data are the mean of 10 observations.

TABLE II. Reproducibility of Recorded X-ray Diffraction Data Taken from the Brass Standard Plate

Scan	Intensity, arbitrary units
1	7.40
2	7.25
3	7.55
4	7.40
5	7.25
6	7.20
7	7.20
8	7.15
9	7.20
10	7.35
Mean	7.30
Standard deviation	+0.13
Coefficient of variation	−1.8%

ment results in satisfactory performance such that monitoring of the intensity of the primary beam is unnecessary. Although, as well known, for greatest precision the best method is counting, the degree of precision of the strip-chart recording is great enough so that this method is also acceptable; its speed makes it particularly desirable.

Further verification of the stability of the instrument was obtained by making two sets of scans of the brass interference ($2\theta = 42.2°$) on each of two separate days. The data are given in Table II, where the statistical analysis indicates a high degree of reproducibility.

Tests for air scatter and Compton effect indicated that corrections for such effects were of a minor order and need not be made. The errors which arise from an asymmetric slit system, discussed by Klug and Alexander [8], were minimized in this work by taking data only at diffraction angles of $2\theta = 18°$ and greater.

Although the diffractometer was designed to be operated on the focusing principle, where the specimen is held at an angle to the primary beam and rotated at half the angular speed of the scanning counter unit, it was desirable to test the operation of the instrument with the specimen held stationary and normal to the primary beam, as in the transmission technique. The tracings for native and decrystallized cottons given in Figure 1 show marked differences in the recorded intensities according to the technique employed. The tracing obtained by the focusing technique displays greater resolution, greater intensity of the 002 interference, and absence of 021 interference. The transmission tracing is essentially identical to that which would be obtained by the radial photometering of a Debye-Scherrer powder pattern and is the expected result. The tracing produced by the focusing technique, however, is unusual in that the 021 interference is absent—it more nearly resembles a photometer tracing taken along the equator of the fiber pattern. This effect is attributed to a selective orientation of the particles in the specimen disc and will be discussed later.

Because of the greater resolution and higher intensity of the characteristic cellulose I interferences produced by the focusing technique, it was selected as the preferred method to be used in this work. This was substantiated by correlations computed on the data obtained by the two methods.

Specimen Preparation

Except for the vibratory ball-milled materials, samples were prepared for use in the diffractometer

by first grinding in a Wiley mill to pass a 20-mesh screen. Discs 0.5 in. in diameter were prepared by compressing 0.125 g. of the ground material in a mold under a pressure of 25,000 lb./sq. in. Disc thickness was measured with a dial-type thickness gauge. After the disc was pressed flush with the surface of the specimen holder, the sample was scanned over the range $2\theta = 6°$ to 30°. The specimens were normally examined by the focusing technique for which the instrument was designed. For examination by transmission, a stationary holder was substituted for the regular rotating holder at the apex of the quadrant.

Grinding of the samples in a sharp, well-adjusted Wiley mill to obtain a more compact specimen and to randomize crystallite orientation was found not to have much effect on the crystallinity itself, as revealed by x-ray examination. There was no decrease in the intensity of the crystalline interferences of purified cut cotton, but there was a slight rise in the amorphous scattering between the $10\bar{1}$ and 002 peaks ($2\theta = 18°$ to 20°). This may be due to a slight reduction in the degree of crystalinity, showing agreement with the findings of Nelson and Conrad [13], who on the basis of the acid hydrolysis method reported a decrease in crystallinity upon grinding in the Wiley mill.

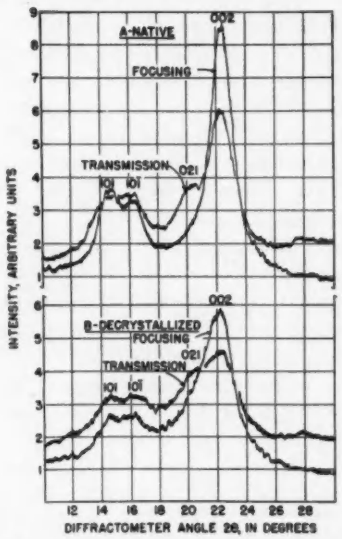

Fig. 1. Comparison of tracings made from (A) native and (B) decrystallized cottons by focusing and transmission techniques.

Several factors in preparing the sample disc influenced the results obtained. Sharpness and proper clearance of the blades of the Wiley mill were found to be important in keeping the effect of grinding to a minimum. Use of a binding or cementing agent, such as gum arabic, caused an undesirable reduction in the intensity of the cellulose interferences; however, since discs prepared without the gum had good cohesion, this effect could be avoided. A 4-hr. extraction of raw cotton samples with 95% ethanol in a Soxhlet apparatus, followed by a water-wash prior to grinding, resulted in thinner discs and more highly resolved tracings with greater peak heights; this treatment was not required for chemically treated or purified cottons. The amount of pressure used in preparing the discs influenced disc thickness principally and peak height only slightly. This can be seen in Figure 2, where, although at pressures above 18,000 lb./sq. in. the recorded height of the 002 interference showed little change, disc thickness

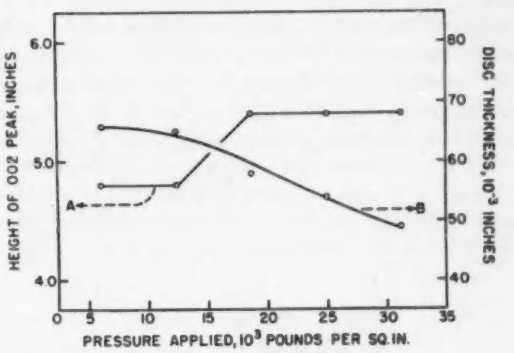

Fig. 2. Effect of amount of pressure applied to sample on peak height and disc thickness. Raw Deltapine Cotton, 0.125-g. sample.

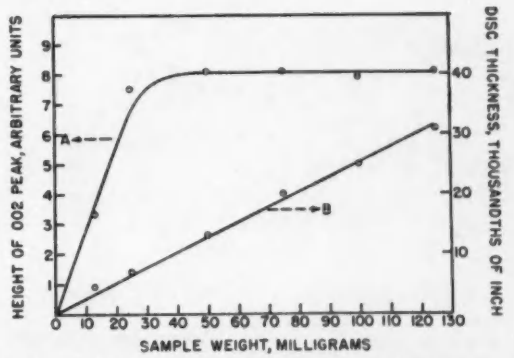

Fig. 3. Effect of sample weight on peak height and disc thickness. Purified cut cotton pressed at 25,000 lb./sq. in.

decreased continually as pressure was increased. When sample weight was increased, the disc thickness increased regularly, but little change in peak height occurred above a sample weight of 0.040 g. (Figure 3).

The above data indicated that conditions for optimum intensity of the diffracted radiation were satisfied with a sample weighing no less than 0.050 g.; however, a weight of 0.125 g. was chosen for use because it gave nearly optimum thickness for examination by the transmission technique, if desired.

Planar Orientation of Particles

Microscopic examination of the particles of ground cotton clearly showed varying short lengths of fibers which have been cut across the fiber axis. In such fiber fragments, the paratropic planes of the cellulose crystallites are still parallel to the fragment surface. The diatropic planes of the crystallites are also in the same relationship to the axis as in the uncut fiber; i.e., they are predominantly normal to it. When the ground particles are pressed into sample discs, the majority of the particles are oriented by the applied pressure such that the long axes lie preferentially parallel to the surface of the disc; in all other respects, particle orientation is random. Figure 4 illustrates the position of the 021 plane in the unit cell and its relation to the sample surface and to the primary beam. It may be seen that with the disc in the transmission position the 021 plane

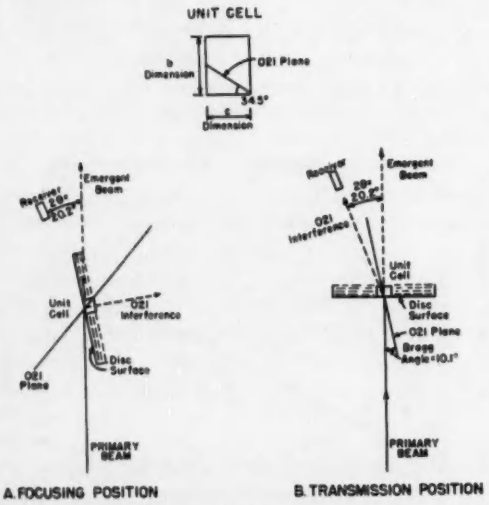

Fig. 4. Relation of the 021 plane to the unit cell, to the sample surface, and to the primary beam.

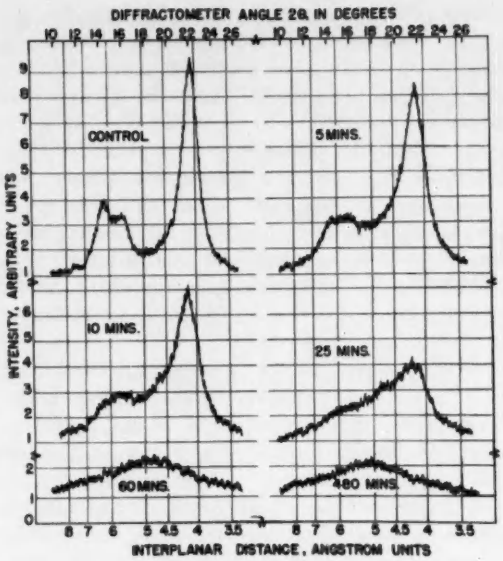

Fig. 5. Radial tracings of cotton ground in a vibratory ball mill.

(Bragg angle = 10.1°) diffracts radiation which can be detected by the scanning element. On the other hand, in the focusing position, the diatropic planes are so oriented that radiation diffracted by them is not contained in the plane of the scanning element and no recording is made of those interferences.

The region near $2\theta = 18°$ is then left clear for evaluation of the amorphous contribution which in totally amorphous cellulose is at its maximum at this angle (Figure 5). Irrespective of the angular distribution of the paratropic planes in the sample about a normal to the sample surface, radiation is diffracted from them in the horizontal plane containing the scanning element.

The x-ray diffraction tracings are thus subject to sample preparation errors, to fluctuations inherent in the primary radiation and in the counting and recording processes, and to slit geometry errors. With proper sample pretreatment and optimum conditions for preparing specimen discs, the over-all variation was comparable to that reported by Klug [7] for mechanical mixtures of highly crystalline materials.

Other Evaluation Techniques

Density was determined by the density gradient column method as described by Orr and coworkers [17]. Acid hydrolysis crystallinity was determined

by the method of Philipp, Nelson, and Ziifle [19], and leveling-off degree of polymerization (LODP) by the technique of Nelson and Tripp [14]. Regain measurements, approached from the dry side, were made by desiccation (over P_2O_5) of the samples at room temperature and subsequent conditioning for one week over a saturated magnesium acetate solution at 70° F. (RH of 65%). The infrared crystallinity index values were obtained from infrared absorbance measurements in accordance with the technique described by O'Connor and coworkers [16].

Cotton Samples and their Preparation for Examination in the Diffractometer

The cotton samples used in this work are described under four groupings. First is a cotton sample which was artificially cut to simulate linters and commercially purified by heating with dilute caustic solution (2%) under pressure, followed by a bleach. This sample was used in studying the instrumental factors. Second, a set of samples derived from one lot of raw cotton yarn and representing different degrees of crystallinity was obtained by treatment with ethylamine in the manner described by Segal and others [12, 20]. The untreated yarn was designated Sample A; Sample B was a part of the same, kier boiled (2% caustic); Samples C, D, E, and F with reduced crystallinities were obtained from Sample A by treatment with aqueous solutions of 70, 75, 80, and 100% ethylamine respectively. Sample G was a portion of Sample F that had been boiled in water for 2 hr. This set of samples was used as a calibration standard for the x-ray method against other accepted chemical and physical methods. The third sample was a Deltapine cotton which had been ground for periods of 5, 10, 25, 60, and 480 min. respectively. These samples were used in justifying the use of the intensity at 18°, 2θ, as a measure of the proportion of the amorphous cellulose. The fourth group included 28 samples of untreated and decrystallized samples which were taken at random to further evaluate the experimental error of the method.

Results and Discussion

On the second series of samples, which were kiered and decrystallized as described above, determinations were made of acid hydrolysis crystallinity

TABLE III. Results of Physical and Chemical Measurements on Untreated, Kiered, Decrystallized, and Water-Boiled Cotton Yarns

Sample	Treatment	AHCr, %	LODP glucose units	Density, g./cc.	Moisture regain, %	Infrared crystallinity index	Diffractometer measurements, cm.		X-ray crystallinity index, %
							I_{am}	I_{002}	
A	Untreated cotton yarn	84.0 ± 2.0	219	1.544	8.57	2.28	4.6	22.1	79.2 ± 0.5
B	Portion of A, kier boiled	88.6 ± 1.4	230	1.544	8.72	3.08	5.2	24.7	79.0 ± 0.7
C	Portion of A, treated with 70% ethylamine	63.2 ± 4.0	180	1.540	9.91	1.52	5.2	18.9	72.5 ± 1.6
D	Portion of A, treated with 75% ethylamine	38.6 ± 3.0	161	1.539	10.34	1.16	5.7	18.2	68.7 ± 0.4
E	Portion of A, treated with 80% ethylamine	24.0 ± 3.4	149	1.534	10.56	1.12	6.0	17.1	64.9 ± 0.0
F	Portion of A, treated with 100% ethylamine	27.5 ± 5.1	140	1.532	10.83	0.93	6.1	16.6	63.3 ± 0.5
G	Portion of F, water-boiled 2 hr.	84.2 ± 2.1	153	1.540	9.89	2.19	5.3	22.1	76.0 ± 0.4
	Standard error of estimate, %	1.41	3.92 (1.17)	1.93	2.45 (1.42)	2.69			
	Coefficient of correlation with crystallinity index	0.98	0.79 (0.99)	0.95	0.92 (0.97)	0.90			

(AHCr), leveling-off degree of polymerization (LODP), density, and moisture regain, these being properties generally accepted as being associated with degree of crystallinity [14, 19, 20, 23]. Infrared absorption measurements were made also, since O'Connor and coworkers [16] consider that the infrared spectra may be used to measure crystallinity.

The results (Table III) show, in general, the changes anticipated. The untreated yarn showed an acid-hydrolysis crystallinity of 84% which was slightly increased by kier boiling. Treatment of the raw yarn with increasingly more concentrated solutions of ethylamine gave products of progressively lower AHCr within limits of experimental error. Boiling the 100%-ethylamine treated sample with water for 2 hr. resulted in what appears to be complete restoration of the initial crystallinity. The changes in acid-hydrolysis crystallinity were very closely paralleled by changes in the infrared crystallinity index, in good agreement with the earlier findings of O'Connor and coworkers [16].

The trend in the LODP values was also highly consistent with the manner of treatment. The value 219 for the untreated sample increased slightly to 230 due to kier boiling and then decreased progressively as the concentration of ethylamine increased. Boiling Sample F in water (Sample G) caused a small but definite increase.

The trends in density, AHCr, and LODP values are parallel, with the exception that kier boiling failed to cause any noticeable increase in density. Water boiling caused a small but definite increase in density.

The trend in moisture regain data agrees well with that for the density values. The increase in value with increasing concentration of ethylamine is entirely in line with expectation, as is the decrease following water boiling.

Taken as a whole, the data in the first five columns of Table III show highly concordant results and indicate changes of the properties related to the degree of crystallinity. The data in this table will be referred to again after consideration of certain x-ray measurements.

Selection of an Equation for X-Ray Crystallinity Index

If the beam intensity along the radius of the radiation diffracted by a randomized, finely cut (Wiley mill) sample of cotton is traced by means of the x-ray diffractometer, curves such as those obtained in Figures 1A and B will be obtained. Figure 1A shows the curves for unmodified cotton, while Figure 1B shows corresponding curves for the decrystallized sample. Comparison of the corresponding curves for A and B shows that the valley about $2\theta = 18°$ is considerably raised and the peaks at $2\theta = 14.4$, 16.0, and 22.8° are considerably lowered. As shown in Figure 5, the peaks and valleys almost completely disappear in the course of vibration ball mill grinding at which crystallinity has almost, if not entirely, disappeared. The problem at hand, therefore, involves selection of suitable measures to reflect the changing proportions of crystalline and amorphous components. Two obvious procedures are available: the areas beneath suitable regions of the curves could be integrated after appropriate corrections and adjustments, and the height of certain maxima and minima above the background along the curves could be measured and mathematically related. The former procedure has been undertaken by a number of investigators [4, 9, 15], while others have chosen the latter procedure [1, 2, 6], and some have used a combination of the two [4].

After detailed consideration of the data the discussion of which would be too extensive to present here, the following relation, representing the second procedure and designated "Crystallinity Index," was selected as most promising:

$$\mathrm{CrI} = \frac{(I_{002} - I_{am})}{I_{002}} \times 100$$

In this equation, where CrI expresses the relative degree of crystallinity, I_{002} is the maximum intensity (in arbitrary units) of the 002 lattice diffraction and I_{am} is the intensity of diffraction in the same units at $2\theta = 18°$. This equation is similar to Ingersoll's "radial intensity ratio" [6], except that Ingersoll, working with cellulose II and data obtained photographically, used $I_{10\bar{1}}$, the height of the $10\bar{1}$ peak, instead of I_{002}, and I_{am} was the height of the minimum between the 101 and $\bar{1}0\bar{1}$ interferences. The suitability of peak height measurements as against integrated areas for applications such as this has been shown to be satisfactory not only by Ingersoll, but also by Hermans and Weidinger [4], Clark and Terford [2], and Palmer and coworkers [18].

Examination of each of the samples listed in Table III resulted in curves whose measured heights above a base line at $2\theta = 18.0$ and 22.8° gave the values

I_{am} and I_{002} respectively. It will be seen that the values of CrI show a downward trend which parallels closely the other measures generally associated with crystallinity changes.

Simple correlation analyses were run with each measure, giving the adjusted correlation coefficients shown in the bottom row of the table. The results ranging from 0.90 to 0.98 are most favorable, indicating in all cases less than one chance in a hundred that so high a correlation would be found purely by chance.

The standard errors of estimate of the x-ray crystallinity index computed from acid hydrolysis crystallinity and density are lower than those from the other methods (Table III).

LODP and moisture regain results of Sample G, the recrystallized sample, showed the greatest discrepancy. The coefficient of correlation and standard error obtained in this case are enclosed in parentheses in Table III.

Since the infrared technique used in obtaining infrared values presented in this study is still preliminary in nature, it is encouraging that such a high correlation with the x-ray values was found to exist.

When comparing data from the present empirical x-ray method to those based on the kinetics of cellulose hydrolysis, large discrepancies may result because of the recognized errors associated with such rate processes. This is illustrated in Figure 6, which shows the least square relationship between acid-hydrolysis crystallinity and crystallinity index as given in Table III for the calibrating standards, Samples A–G.

The greatest departure from the regression line is seen to be at the low crystallinity end of the plot where, as is well known, the precision of the acid hydrolysis method is at its least. The standard error of other samples as taken from the curve of the calibration samples is 3.7.

Summary

Cotton cellulose samples for estimation of crystallinity by x-ray are easily prepared in the form of discs of 0.5-in. diameter by grinding the fiber in a Wiley mill to pass a 20-mesh screen and then compressing 0.125 g. of the material in a mold under a pressure of 25,000 lb./sq. in.

With data taken from the diffractometer operated by the focusing technique, the intensities of the 002 interference of cellulose I and the amorphous background at $2\theta = 18°$ give a useful indication of the relative crystallinity of the sample when substituted into the empirical relationship.

The present empirical x-ray "crystallinity index" affords a considerable saving in time when many modified and unmodified cotton samples are to be evaluated for differences in their crystallinity.

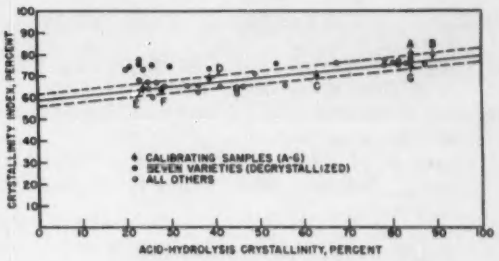

Fig. 6. Relationship between crystallinity indices and acid-hydrolysis crystallinities for the calibration standards, Samples A–G. Points are given also for other samples for which comparable data were available. The dashed lines represent twice the standard error about the regression line of the calibration samples.

Acknowledgment

The authors wish to acknowledge the contributions of Dr. F. Forziatti of the National Bureau of Standards for grinding cotton in the vibratory ball mill; Mr. R. S. Orr for the density determinations; Dr. M. L. Nelson for the determinations of acid-hydrolysis crystallinity; Mr. T. Mares for the LODP measurements; Miss H. M. Ziifle for calculations and drawings; and Mrs. E. F. DuPré and Miss E. R. McCall for the infrared measurements.

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An Instrument for Study of Friction and Static Electrification of Yarns[1,2]

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Abstract

An instrument for measuring the friction and static electrification of moving yarns has been designed, constructed, and tested. The instrument allows measurements to be made on yarns over a wide range of speeds under a practically constant predetermined tension. The instrument also has applications for measurements of certain yarn mechanical properties. Some static electrification and friction studies are discussed. These have revealed some interesting effects which are not yet fully understood, such as reversal of the sign of transferred charge with change of speed and the unusually plastic behavior of nylon yarns in moving contact with surfaces.

Introduction

In studying the friction and static electrification behavior of moving yarns, the yarn tension must be known and controllable. Various devices and methods have been described from time to time for controlling yarn tension. These generally add tension to the take-off tension of the yarn from its package in such a way that the final tension is more or less constant but has a relatively high value. The instrument to be described here enables measurements to be made at constant tension in ranges below the yarn take-off tensions.

[1] Presented at the September 1958 meeting of The Fiber Society, Montreal, Canada.

[2] Publication Number 54 of the Chemstrand Research Center.

Description of the Instrument

The instrument is diagrammed in Figure 1. The yarn leaves the package through a guide and passes through a simple friction tensioning device which keeps the minimum tension on the yarn high enough that the yarn will not slip on the rolls. The yarn passes around the first pair of draw and separator rolls A and B several times, down around a pulley, and up and around the second pair of draw and separator rolls, from which it is drawn away by a wind-up device (not shown). The two large rolls A are driven by a variable speed motor C. The speed of this motor is determined by a setting of the speed controller E, working in conjunction with tachometer D. The two pairs of rolls are geared together through a differential F.

The device operates in the following manner. If, for example, the weight of the pulley at the bottom of the yarn loop H is sufficient to cause the yarn to stretch as it enters into the loop, the pulley will drop. The pulley is connected to a Microsyn[2] position detector by means of a lever arm. When the pulley drops, the Microsyn produces an electrical signal which is amplified by a servo amplifier and then turns the servo motor G. The servo motor turns the differential in such a way that the first roll is slowed with respect to the second and thus takes up the slack in the yarn loop.

If, on the other hand, the yarn shrinks, the opposite action takes place; the pulley is thus kept at an equilibrium position such that the lever arm connecting the pulley to the Microsyn is always maintained level. The tension on the yarn is then due only to the weight of the pulley plus whatever additional weight is added by hanging various weights directly under the pulley on a hook. The yarn tension is also affected by the frictional properties of the pulley.

Figure 2 shows a photograph of the instrument.

Performance of the Instrument

In analyzing the performance of the instrument, two types of measurements were made. A diagram of the method is shown in Figure 3. The average tension on the yarn was measured by means of an unbonded strain gauge upon which is mounted a pulley. The yarn leaving the loop was passed over this pulley and then down to the second roll of the instrument. The strain gauge was calibrated directly by hanging weights on the pulley at the bottom of the loop when the yarn is not moving. The tension of the yarn was then measured at various speeds and with loads from 1.0 to 200 g. on the bottom pulley. The increase in tension of the yarn in motion over the tension of unmoving yarn was found to be independent of the load, but not of the speed. The increase in tension due to yarn speed is plotted in Figure 4.

The variation about the average tension was measured, using the strain gauge in the same manner as before, except that the alternating-current component of the output from the strain gauge was amplified and recorded on an oscillographic re-

[2] Manufactured by Doelcam, Boston, Massachusetts.

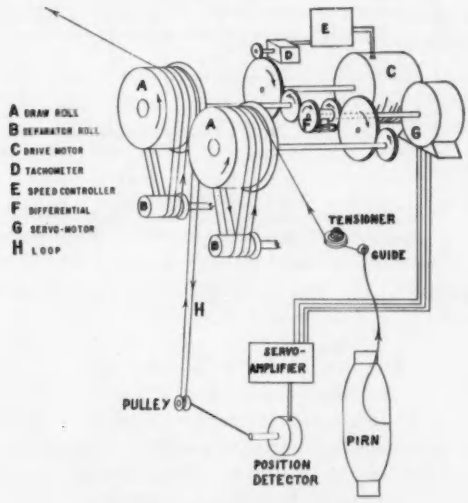

Fig. 1. Constant yarn tension device.

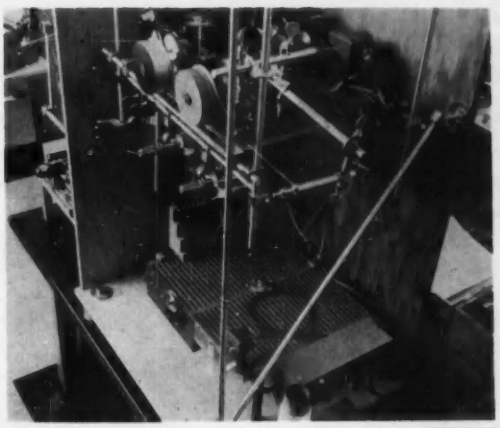

Fig. 2. Photograph of actual instrument.

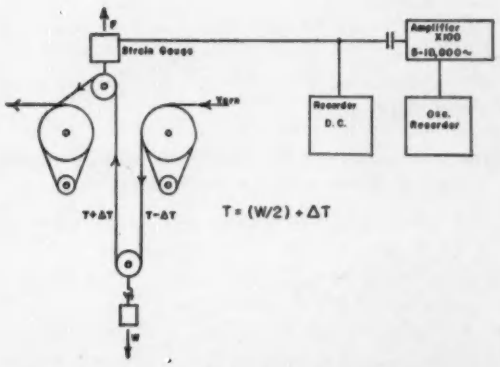

Fig. 3. Set-up for testing instrument performance.

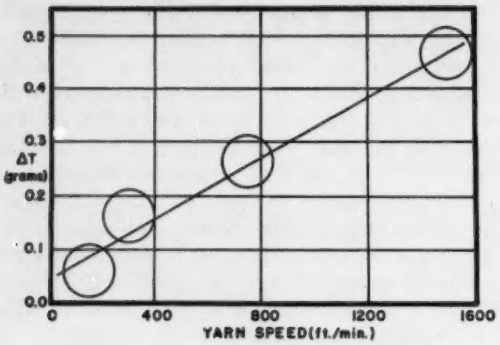

Fig. 4. Tension increase versus yarn speed.

corder. The tension variations were found to depend upon load and speed in an irregular manner. Root-mean-square values of the variation observed range from ±0.003 to ±0.018 g. Most of the variation observed can be accounted for by vibrations in the rapidly rotating pulley attached to the strain gauge. The vibration of the freely rotating pulley when yarn is not passing over it causes a varying output of the strain gauge of about the same magnitude and frequency as when yarn is passing over it. A similar effect may be expected from the pulley used at the bottom of the loop, so that practically all of the tension variation can be attributed to these two pulleys. The pulleys used in the performance test are specially designed and machined to reduce eccentricity, and are then carefully balanced.

The ranges of tension and speed for the instrument are very wide. Tensions from 0.7 g. to several hundred grams, and speeds from extremely low, say 10 ft./min., up to as high as 2000 ft./min. have been used.

The instrument has performed very satisfactorily with various types of yarn ranging from 15-den. nylon monofilaments to heavy nylon tire yarns and twisted staple yarn.

Speed or Frequency Limitations of Measurements Made with the Instrument

The strain-gauge pulley assembly pictured at the top of Figure 3 and used to measure the yarn tension in analyzing the instrument had a resonant frequency of about 160 cycles/sec. Measurements of the yarn-tension variations such as might be desirable in a friction measurement would involve the use of a similar device having a characteristic

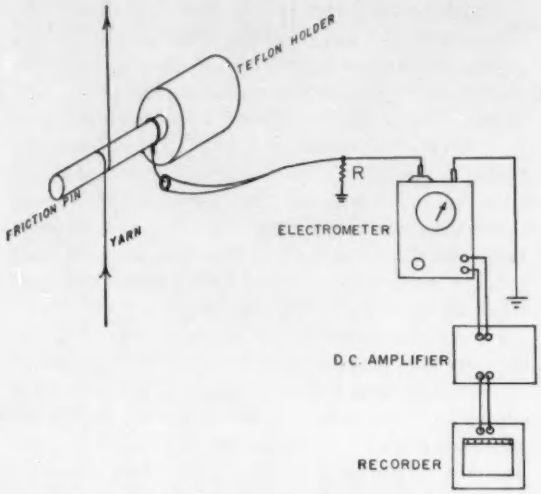

Fig. 5. Method of measuring static electrification.

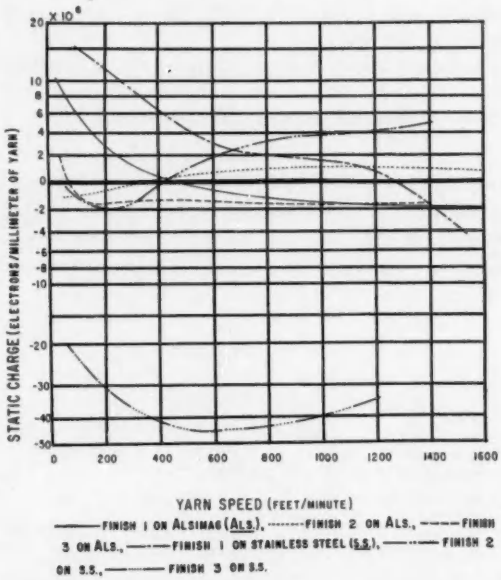

Fig. 6. Static charge transferred to yarn from cylinder as a function of yarn speed.

resonant frequency. For 98% accuracy, any measurement of tension variations should be limited to an upper frequency of roughly one-tenth of the resonant frequency of the transducer, that is, about 16 cycles/sec. in this case. Tension variations at frequencies higher than this cannot be determined with accuracy. Of course, average tensions can be

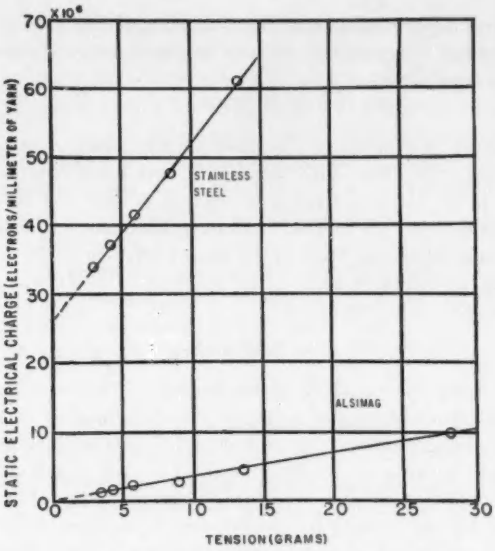

Fig. 7. Static charge transferred to yarn from cylinder as a function of yarn tension; 40/13 nylon yarn, 1000 ft./min.

accurately determined at any yarn speed. In the friction measurements which will be described later, the average tension was measured in all cases.

Measurement of Static Electrification

Figure 5 shows a method used for measuring the static electrification of yarns at various speeds and tensions by use of this instrument. The upgoing portion of the loop is passed around a cylinder of the friction material. The cylinder is held in an insulating holder, and the current from the yarn to the cylinder as they rub together is passed through a resistor R. The resulting voltage is measured and recorded with the aid of an electrometer.

Figure 6 shows some typical results obtained by this method. These curves were obtained from continuous-filament nylon yarns of the same type with different surface coatings applied. All conditions were kept the same, and the charge transferred to the cylinder is plotted against the yarn velocity. Cylinders of the ceramic material Alsimag[4] and of stainless steel were used. The shape of these curves, and particularly the change in sign as the yarn velocity increases, pose some very disturbing questions about the charge-transfer process.

[4] Product of the American Lava Corporation, 219 Kruesi Building, Chattanooga, Tennessee.

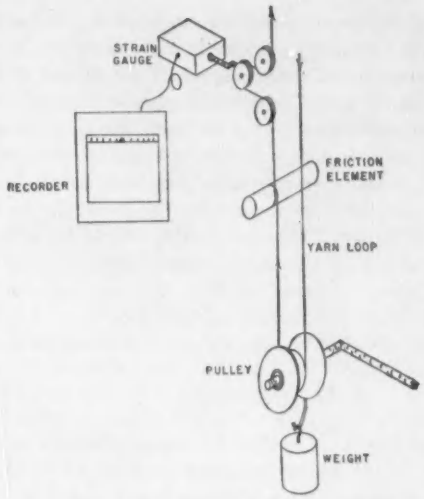

Fig. 8. Method of measuring yarn friction.

The results found here are similar to results obtained by Gonsalves and Dongeren [1] by a similar method.

Figure 7 demonstrates how the charge transferred varies with the tension of the yarn entering the cylinder. The charge transferred to Alsimag and stainless steel cylinders is plotted against the yarn pretension. These curves indicate that problems of static electrification might be reduced at least with nylon by using insulating materials throughout as guides and by keeping the yarn tensions at low values. The fact that the static electrification is apparently linear in relation to the yarn pretension may throw some light on the charge-transfer process.

Measurement of Yarn Friction

Figure 8 shows the method used with the instrument in making the friction measurements presented here. The yarn input tension is determined by the weight on the bottom pulley and by the friction of that pulley. The yarn tension leaving the friction object is measured by the strain gauge and pulley arrangement shown. A recorder is useful in this work.

The data presented in this paper have been corrected for the friction of both the bottom pulley and the strain-gauge pulleys. The friction of the particular set of pulleys used in the friction measurements varied with both speed and load. The accuracy of the friction-coefficient values is greater

in the higher input-tension regions. The method used in obtaining the friction data shown here is not suitable for detecting small differences in friction which are of interest in certain studies. It is theoretically possible to measure the friction using only the one pulley at the bottom of the loop to produce the input tension; the output tension is then measured by measuring the force on the friction cylinder. This procedure would reduce the uncertainty of the measurement considerably and give more accurate results. An analysis of this method has not as yet been completed.

Equation 1 gives the classical Amonton's law of friction

$$F = uW \tag{1}$$

where F = force of friction, u = coefficient of friction, and W = normal force or load. The coefficient of friction is a parameter whose value depends upon the nature of the materials in rubbing contact. An empirical expression, Equation 2, fits friction data more exactly.

$$F = aW^n \tag{2}$$

where a and n = parameters. The exponent n and the coefficient a are parameters dependent upon the nature of the materials in rubbing contact, the shape of the objects in contact, and the shape or nature of the surface asperities on the objects. The explanation for this nonlinearity is that the force of friction is proportional to the area of true contact of the two bodies. The area of true contact is usually less than the apparent area of contact owing to the presence of surface asperities. As more normal force is applied, the area of true contact increases as some power of the force.

Current theories of friction following the ideas of Bowden and Tabor [2] are that the force to break an area of true contact is equal to the shear strength of the weakest material involved in the contact area, times the area of true contact, as in Equation 3.

$$F = AS \tag{3}$$

where A = area of true contact and S = shear strength of weakest material in contact. The expression "weakest material" is used here because in some circumstances the yarn or the friction object could be coated with a substance of considerably lower shear strength than that of either of the other two bodies.

The true area of contact can be related to the average pressure over the contact and the load or normal force at the contact in the manner shown in Equation 4.

$$\bar{p} \equiv W/A \tag{4}$$

where $\bar{p}$ = average pressure in the area of true contact. From Equations 1, 3, and 4 one can obtain the classical friction coefficient. This quantity is then the ratio of the shear strength of the weakest material in the contact to the average pressure in the contacts between the two bodies involved, as expressed in Equation 5.

$$u = F/W = S/\bar{p} \tag{5}$$

Since the materials make contact by the touching of asperities on the surfaces, the deformation of a model asperity can be considered to be the same as the deformation of the smaller actual asperities. A spherical surface is often taken as a model asperity, and many friction studies have been made by rubbing a spherical body against a hard flat-surfaced body.

The equation of the deformation of a sphere against a flat surface has been derived by Hertz [3] for perfectly elastic materials. The average pressure of the contact area between a sphere and a much harder flat object is given by Equation 6, which can be derived from Hertz's result.

$$\bar{p} = (4/\pi)[E/1 - \nu^2]^{2/3}(W/D^2)^{1/3} \tag{6}$$

where E = Young's modulus of elasticity for the softest material, ν = Poisson's ratio for the softest material, and D = diameter of sphere.

A similar equation for the deformation of a cylinder in contact with a flat body can be derived; see, for example, Thomas and Hoersch [4]. A review of this derivation is presented by Timoshenko and Goodier [5]. The equation corresponding to Equation 6 for this case is given as Equation 7.

$$\bar{p} = [\pi E/2(1 - \nu^2)]^{1/2}(W/dL)^{1/2} \tag{7}$$

where d = diameter of cylinder and L = length of cylinder. Note that $\bar{p}$ is now proportional to the load to the one-half power rather than to the one-third power.

If the material is plastic, the Hertzian equation is not followed. For a perfectly plastic solid in contact with a hard object, the average pressure would equal the yield pressure of the material, as described by Equation 8.

$$\bar{p} = P_y(W/D)^0 = P_y \tag{8}$$

where P_y = a constant for the material (yield pressure). The load and the dimensions of the body appear with a zero exponent, and hence disappear; thus $\bar{p}$ is independent of the load, size, and shape of the body. As more and more load is applied to the object, the object conforms to the shape of the harder object, until enough area is in contact between the two objects to exert a reaction equal to the load applied.

For a material that is partially plastic and partially elastic, a power law such as Equation 9 is probably sufficiently accurate to describe the deformation for the purpose here.

$$\bar{p} = hW^m/(dL)^m \tag{9}$$

where h and m = constants depending upon the material and shape of the object and d and L = dimensions of the object. The exponent m in this expression varies from zero for perfectly plastic materials to $\frac{1}{3}$ for perfectly elastic materials, provided the geometry is spherical or ellipsoidal. If a cylinder (such as a fiber) is being deformed against a relatively flat surface, the value for m is $\frac{1}{2}$ for perfectly elastic materials. A semielastic material in the shape of a cylinder would have an m value between zero and $\frac{1}{2}$.

To calculate the force of friction from this expression for the average pressure, Equations 3, 4, and 9 are combined. An expression like the empirical Equation 2 is found where the exponent n of Equation 2 is the equivalent of the exponent $1 - m$ of Equation 10.

$$F = (S(dL)^m/h)W^{1-m} = aW^n \tag{10}$$

where $(1 - m) = n$ and $(S(dL)^m/h) = a$. The exponent n is then 1 for perfectly plastic materials, $\frac{2}{3}$ for perfectly elastic materials of spherical or ellipsoidal shape, and $\frac{1}{2}$ for perfectly elastic materials of cylindrical shape. Crossed cylinders of diameters of near magnitude (diameter ratios less than 8:1 [4]) obey the deformation laws equivalent to spherical or ellipsoidal geometry.

The often-used relationship between output and input tensions of yarn wrapped around a cylinder is often called the capstan equation. It expresses the logarithm of the ratio of output tension to input tension as equal to the coefficient of friction times the angle of wrapping of the yarn on the cylinder, as shown in Equation 11. It is derived by integration of the differential form of Equation 1.

$$\ln (T_o/T_i) = u\theta \tag{11}$$

where θ = angle of wrap of yarn around the cylinder, T_o = tension of outgoing yarn, and T_i = tension of ingoing yarn.

Howell [6], using Equation 2 rather than Equation 1, derived a modified capstan equation, shown in Equation 12.

$$\begin{aligned}\ln (T_o/T_i) &= (1/1 - n) \ln [1 + (1 - n)a\theta(\rho/T_i)^{1-n}] \\ &\cong [a(\rho/T_i)^{1-n}]\theta\end{aligned} \tag{12}$$

where ρ = radius of curvature of the cylinder. The second expression of Equation 12 can be used for an approximation in regions where the second term in the expression is much less than unity. Note the similarity between Equation 11 and the last expression of Equation 12. The logarithm of the tension ratio divided by the angle of wrap is equivalent to the classical coefficient of friction. When the logarithm of this quantity is plotted against the logarithm of the input tension, a straight line will be found if Howell's equation is obeyed. The slope of the line gives a value for n. The constant a can be found from the intercept.

This procedure can be seen more clearly by taking logarithms in Equation 12 to obtain Equation 13. The exponent n is related to the plasti-elastic behavior of the yarn material, and the constant a is related to the dimensions of the yarn material, the mechanical properties of the yarn material, and the lubricant material, if any.

$$\begin{aligned}\ln [\ln (T_o/T_i)/\theta] &= \ln (a) + (1 - n) \ln (\rho/T_i) = \ln (u)\end{aligned} \tag{13}$$

Figure 9 is a plot of the variables in Equation 13 for 40/13 semidull nylon yarn wrapped 360° around a ceramic cylinder, with speed as a parameter.

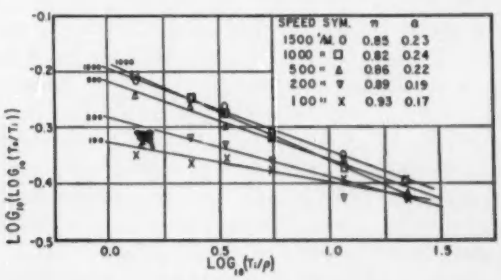

Fig. 9. Friction of a multifilament yarn as a function of yarn tension and speed; 40/13, 1/2 Z, S.D. nylon on Alsimag draw pin.

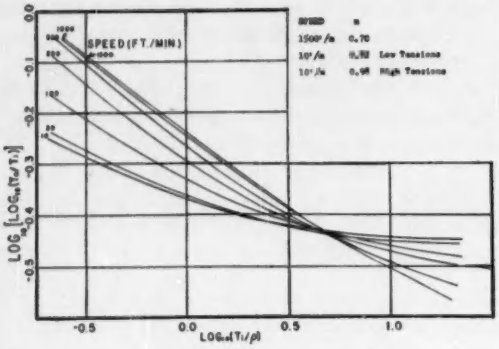

Fig. 10. Friction of a monofilament yarn as a function of yarn tension and speed; 30/1 S.D. nylon on Alsimag draw pin.

Straight lines are found for each speed; the values of the exponent n are shown in the table in the upper right hand corner of the graph.

Howell considered that a perfectly elastic material should have an exponent equal to $\frac{2}{3}$ from the equation of deformation of spheres or crossed cylinders. A better equation to use [4] would be that of the deformation of a cylinder on a flat object, since the fiber diameter is so much smaller than that of the cylinder upon which it is rubbing. If it turns out that the cylinder-plane geometry is dominant, then the exponent should approach $\frac{1}{2}$ instead of $\frac{2}{3}$ for elastic materials, as has been implied earlier by other workers, such as Baird and Mieszkis [7].

If the exponent of $\frac{1}{2}$ is correct, it should be pointed out that the experimental values indicate that all yarn materials are behaving more plastically than has been thought, since the values obtained in experiments on nylon here reported and by other workers on nylon range from 0.70 to 1.0. Values of the exponent for other yarn materials including natural fibers are in the same range as the values for nylon. Polymers like nylon in the oriented state are usually considered quite elastic, and deformation experiments of spheres such as those by Pascoe and Tabor [8] indicate that even unoriented nylon behaves very nearly elastically. Considerable discrepancies thus exist between the elasticity deduced for nylon from yarn friction experiments and with friction and penetration experiments with spherical sliders and penetrators in bulk nylon.

Archard [9] considered the case of the deformation of smaller asperities on the surface of larger asperities and found that the exponent increases and approaches unity as the complexity of the model increases. He has demonstrated experimentally that the exponent changes as a function of load when these multiple asperities are present on the surface. For larger loads where the asperities are pressed out more or less flat, the exponent approaches the value expected from the bulk shape of the sample material.

Figure 10, which shows the friction of nylon monofilament as a function of speed and load, indicates that the Archard effect is probably not always the dominant effect in yarn friction. Here the data indicate that in the low-speed region the exponent increases to nearly unity as the load increases, which is just the opposite of the effect predicted by Archard. The cause of this effect is believed again to be due to the viscoelastic behavior of the nylon, in that considerable permanent deformation probably occurs at low speeds and high loads.

Rubenstein [10] also has found that n decreases with increasing yarn speed. Rubenstein measured n as a function of cylinder temperature also, and found that n increases with increasing temperature and that n reached unity for nylon at a temperature of 78° C. The change in n with speed then is not due to an increase in temperature of the materials due to frictional heating, since the two effects are opposite in trend. The decrease in the exponent also cannot be due to the presence of a viscous film, since Hansen and Tabor [11] have found the exponent to be independent of the velocity in experiments with oil-lubricated yarns. The cause of the effect of speed upon the exponent in the Howell equation of friction is then unanswered. It is probably an effect of the viscoelastic properties of the yarn material.

Use of the Instrument for Mechanical Measurements

The instrument can be used with slight modifications for the measurement of certain mechanical properties of moving yarns. It is of special interest in that the elongation of yarns can be measured in very short time intervals.

For the determination of stress–strain properties of yarns, the rate of rotation of the differential or of the servo motor must be measured. The ratio of the rotation of the differential to the rotation of the rolls is a measure of the strain of the yarn under a constant stress for the length of time the yarn is

in the loop. If there is 1 ft. of yarn in the loop and the yarn speed is 1500 ft./min., the yarn is in the loop for 0.04 sec. The yarn is then subjected to the tension in the loop for that period of time, and it will stretch a certain amount under those conditions. By use of various loads on the yarn, a stress–strain curve can be plotted point by point. This stress–strain curve would approximate a stress–strain curve obtained on a conventional tester at a very high rate of elongation. The modulus measurement is, strictly speaking, a short-time creep measurement.

The modulus measurement has been tested as a possible method and appears feasible, but there is nothing to report on the preliminary results using this technique at this time.

If the instrument is to be used for searching for variations in elastic modulus or compliance of yarn, the yarn speed is limited by the resonance vibration of the weight and pulley hanging on the elastic yarn. The frequency of this resonance depends on many factors. In the very severe case of 15-den. hosiery yarn at .1% extension, the maximum scanning speed is 20 ft./min. for 98% accuracy. An electrical damping control is incorporated in the servo amplifier and is used to prevent the resonance oscillation. As the yarn speed is increased, the instrument gives the modulus as the average of longer and longer lengths of yarn. At the high speeds that would be used to obtain the high-extension velocity modulus, the instrument would, of course, give only average values for very long lengths of yarn.

Summary

An instrument has been designed and constructed which enables studies to be made on yarn under conditions of controlled tension and speed. The instrument has performed satisfactorily, and its use in static electrification and friction studies has revealed some interesting aspects of these processes. In particular, the mode of charge transfer involved in the change of sign of the charge with yarn speed is yet unknown. Also, it raises a question about the very plastic behavior of materials in the form of yarn in friction experiments in comparison to the nearly elastic behavior of the same materials in penetration and friction experiments.

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Partially Carboxymethylated Cotton as an Intermediate for Further Chemical Modification[1]

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Abstract

Cotton can be etherified by treatment with chloroacetic acid and sodium hydroxide solution. The product, a partially carboxymethylated cotton, which retains the original fibrous nature of the cotton, has a number of properties valuable for textile and other uses. In addition, the etherified cotton bears two reactive functional groups—hydroxyl and carboxyl—capable of further chemical modification.

The rate and extent of many reactions with the etherified cotton are greater than with native cotton similarly treated. Further modifications of this cotton derivative are discussed. Among these are salt formation for the preparation of bactericidal and fungistatic finishes, reactions for the introduction of cyanoethyl, carboxyethyl, and graft polyester groups, reaction with epoxy and aziridinyl compounds, and oxidation for the preparation of alkali-soluble textile products.

Introduction

This paper presents a brief report of some of the chemical modifications which have been carried out with partially carboxymethylated cotton as an intermediate. It has been found that this cotton derivative will undergo the typical reactions of cellulose and, through the ether substituent, will take part in many reactions typical of a carboxylic acid. Also, the fiber has become more accessible to many reagents because of the strong swelling characteristics introduced by the hydrophilic carboxyl groups. Because of this unique combination of properties, the rate and extent of many reactions with the etherified cotton are greater than with native cotton similarly treated.

Partially carboxymethylated cotton may be simply prepared by the treatment of cotton fiber, yarn, or fabric with chloroacetic acid and sodium hydroxide [3, 4, 20, 21]. The reaction indicated by the equation

$$\text{Cell—OH} + \text{ClCH}_2\text{COOH} + 2\ \text{NaOH} \rightarrow \text{Cell—OCH}_2\text{COONa} + \text{NaCl} + 2\ \text{H}_2\text{O}$$

is carried out by impregnating the cotton with an aqueous solution of chloroacetic acid followed by treatment with strong sodium hydroxide solution. The product is obtained as the sodium salt of carboxymethylcellulose after normal washing and souring but may be converted to the free carboxyl form by treatment with solutions of mineral acids. Partially carboxymethylated cotton retains the original fibrous nature of the starting material.

New properties are conferred upon the cotton as a result of the chemical modification. The magnitude of the changes effected is a function of the degree of substitution (DS). For example, cotton carboxymethylated to a DS of about 0.1 is highly swellable in water; at a DS of about 0.33 the modified cotton is water soluble as the sodium salt.

Partially carboxymethylated cotton with a DS of about 0.05–0.15 exhibits a number of potentially valuable properties [3]. Among these are a crisp hand with a slightly starched feel; increased moisture regain, water absorbency, and water permeability; increased strength and elongation; increased resistance to soiling from aqueous dispersions and greater ease of soil removal; cation exchange prop-

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[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

erties; and great water swellability. In addition, a new functional group—the carboxyl group—has been introduced, and the fiber exhibits increased receptivity to many other treatments.

Variables in the laboratory preparation of the partially etherified cotton have been extensively investigated and defined. Also, successful runs have been made in the pilot plant, and techniques and methods for commercial production have been suggested [7]. A preliminary cost study has indicated that the process is economically sound [7]. In fact, approximately 1.5 million yards of cotton fabric are currently being carboxymethylated each year for a captive use. Carboxymethylation of textiles, on a commission basis, is offered by a finishing plant [9].

Experimental and Discussion

The presence of two reactive functional groups—hydroxyl and carboxyl—in partially carboxymethylated cotton affords attractive sites for further chemical modification by a number of reagents. Among the types of modification which were investigated were salt formation, esterification, etherification, and oxidation. Examples of these are described in the following sections.

Salts with Bactericidal Properties

The salts of partially carboxymethylated cotton are readily prepared by treatment of the cellulose derivative with solutions containing the desired cation. Several metal salts of the modified cotton have been shown to have rot resistance and other properties [22].

Sterile pulp and paper products have been prepared by incorporation of the phenylmercuric salt of carboxymethylcellulose gel with wood pulp [12]. In processing, the gel becomes an integral part of the paper produced from the pulp and confers antibacterial properties upon the products.

Similarly, with partially carboxymethylated cotton, cations with bactericidal properties have been found to produce fabrics in the salt form with a degree of "self-antiseptic" or "self-sterilizing" properties. The mercuric and phenylmercuric salts of carboxymethylated cotton were prepared by treating the etherified fabric with solutions of mercuric chloride or phenylmercuric acetate and were tested as described below.

Three commonly distributed organisms were chosen to represent different groups of bacteria and fungi. *Escherichia coli,* a nonsporebearing gram negative bacillus, is found in the intestinal tract of animals and man. *Bacillus subtilis,* a gram positive aerobic bacillus, is a saprophyte that is found commonly in soil, dust, air, etc.; it is similar to the organisms that cause gas gangrene in that it can form spores, which are harder to kill than vegetative forms. *Aspergillus niger* is a common mold, more likely to attack cotton than man, but it has been found in ear infections. For each organism, the growth from two slants of media was suspended in 10 ml. of sterile distilled water; 0.05 ml. of the suspension was used to inoculate small squares of previously autoclaved fabrics.

To find the effect of the treated fabrics on these microorganisms, the usual tests, such as the halo test, were not used since it was desired to ascertain whether the cloth would be self-sterilizing. Therefore the following tests were devised.

In one test, the cloth was scraped with an inoculating needle 5 min. after its inoculation and the scrapings streaked onto nutrient agar and onto "Brewer's Anaerobic Medium" (Difco).[3] The latter, since it contains sodium thioglycollate, can combine with mercury salts carried on the scrapings and inactivate their effect [16, 17]. The second test was similar to the first except that the organisms were exposed to the effect of the cloth for 1 hr.

In the third test, the suspension of the microorganisms was placed on the fabric, and 1 hr. later the cloth was shaken in a bottle with 10 ml. of sterile water and 3 small glass beads; the wash water was then poured into 10 ml. of double strength "Fluid Thioglycollate Medium" (Difco) or, in the tests with the very aerobic *B. subtilis,* nutrient broth. Duplicate squares of each fabric were tested with each of the three organisms. As a control of this test, a similar washing was performed on uninoculated cloth; the solutions were poured into inoculated broths to determine whether any toxic salts would be carried over to prevent growth. Unfortunately, it was found that enough mercury was carried over in the washing to prevent the growth of *B. subtilis* in nutrient broth and of *A. niger* in thioglycollate. For this reason, the test is limited to reveal only inhibition of growth, or "stasis," of these two organisms, but it can show killing action on *E. coli.*

[3] The mention of trade products and firms does not imply their endorsement by the U. S. Department of Agriculture over similar products or firms not mentioned.

TABLE I. Growth of Organisms Scraped from Fabrics After Contact of 5 Min. and of 1 Hr.

Salt	Mercury content, %	DS of cloth	Growth of organisms*					
			E. coli		*B. subtilis*		*A. niger*	
			5 min.	1 hr.	5 min.	1 hr.	5 min.	1 hr.
—	0	0.067	4	3	3	0	4	4
PhHg†	0.2	0.005	2	2	1	1	4	4
PhHg	0.37	0.011	0	0	0	0	4	4
PhHg	1.2	0.036	0	0	0	0	0	0
PhHg	3.6	0.067	0	0	1	0	1	0
Hg‡	0.3	0.067	3	0	1	0	3	2

* Numbers indicate estimation of the amount of growth, 4 being heavy growth, 0 being no growth.
† The phenylmercuric salt of partially carboxymethylated cotton.
‡ The mercuric salt of partially carboxymethylated cotton.

TABLE II. Growth of Organisms Washed from Cloth After Contact of 1 Hr.

Salt	Mercury content, %	DS of cloth	Growth of organisms*		
			E. coli	*B. subtilis*	*A. niger*
—	0	0.067	4	2–3	2–3
PhHg†	0.2	0.005	4	0	3
PhHg	0.37	0.011	4	1	1
PhHg	1.2	0.036	0	0	0
PhHg	3.6	0.067	0	0	0
Hg‡	0.3	0.067	0	0	1

* Numbers indicate estimation of the amount of growth, 4 being heavy growth, 0 being no growth.
† The phenylmercuric salt of partially carboxymethylated cotton.
‡ The mercuric salt of partially carboxymethylated cotton.

Tables I and II show the results of tests of the mercuric salt and of the phenylmercuric salt of partially carboxymethylated cotton made with fabrics of various degrees of substitution. With the phenylmercuric salt, where the concentration of mercury in the fabric was over 1%, there was no growth of any organism after 1 hr. contact with the cloth, and there was only a small amount of growth of *B. subtilis* and *A. niger* after 5 min. Even at a concentration of 0.37% mercury there was some inhibition (Table I). Contact for 1 hr. with the mercuric salt of partially carboxymethylated cotton, 0.3% mercury, killed the *E. coli*, prevented the growth of *B. subtilis*, and reduced the growth of *A. niger*.

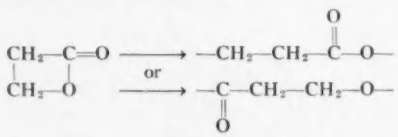
It was concluded from these tests that the phenylmercuric salts of partially carboxymethylated cotton, having a concentration of 1% or more of mercury, have a killing action on some organisms and will prevent the growth of others within 1 hr. of contact. A smaller amount (0.37%) has some, but much less, inhibiting effect, as does the mercuric salt of 0.3% mercury content.

It is believed that the relatively large amounts of mercury were needed because of the slow or "controlled" release of the mercuric cations by the carboxymethylated fabric. That is, only small amounts of mercury are available for use at a given time, but the cations are made continually available by the gradual dissociation of the salt.

This work was not pursued further because of the concentrations of mercury necessary and because of the extreme toxicity of mercury to humans. This toxicity would preclude the adoption of such fabrics for any use in which the material might come into contact with the body.

Treatment with Beta-Propiolactone

The reactions of beta-propiolactone proceed through an opening of the oxetane ring [1].



When cotton is treated with the lactone, it has been shown that either or both reactions may take place to form either carboxyethylcellulose or the hydroxypropionic acid ester. Furthermore, graft polymerization may occur with the lactone reacting with the carboxyl or hydroxyl group just added to the cellulose so that polyester chains are formed [5, 24]. Presumably the formation of the polyester chains is

faster than direct reaction, as shown by the high add-ons which are obtained with relatively few ether linkages to the cellulose.

The treatment of partially carboxymethylated cotton with beta-propiolactone was investigated. Typical of the results are those shown in Figure 1. The add-ons obtained, after exhaustive extraction with acetone to remove unbound polymer and other contaminants, are plotted against the time of treatment with a 10% solution of beta-propiolactone in xylene at reflux. The partially carboxymethylated cotton used was a 7/2 yarn which had a DS of 0.07. For comparison, the graph also includes the curve for samples of mercerized cotton yarn treated under the same conditions.

As shown, the rate of reaction of the beta-propiolactone with partially carboxymethylated cotton was very rapid until about 60% add-on was attained. At this point, there was a sharp break in the curve, with additional treatment leading to practically no increase in add-on. The reaction of the mercerized cotton proceeded at a much slower, but constant, rate for the period of time investigated.

A possible explanation of the more rapid reaction of the carboxymethylated cotton was sought. Possibly, the increased swelling and accessibility of the cellulose in this material is the basis for the increased reactivity. However, it is also possible that the increased reactivity was due to reaction of the lactone with carboxyl groups already present, as well as with the cellulosic hydroxyl groups.

There is no simple method for determining the course of the reaction, but some indication was obtained by examining samples of mercerized cotton and partially carboxymethylated print cloth (DS 0.08) treated with beta-propiolactone as in the previous experiment. These samples had add-ons of 32.6% and 76.8% respectively. They were saponified by treatment with 2% aqueous sodium hydroxide solution at 95° C. for 3 hr. This saponification cleaved the ester linkages, leaving only the substituents which were bound through ether linkages [24]. Carboxyl determinations on these saponified samples were run. It was found that the mercerized cotton had been carboxyethylated to the extent of 0.05 groups per anhydroglucose unit. This represents a weight gain of about 2% out of the 32.6% gain, so it is evident that only a small proportion of the reaction was by direct etherification of the cellulose. The carboxymethylated cotton, which originally contained 0.08 carboxymethyl groups per anhydroglucose unit, was found to have a content of 0.12 groups or a gain of 0.04 groups per anhydroglucose unit. Once again, most of the 76.8% gain was by esterification rather than etherification.

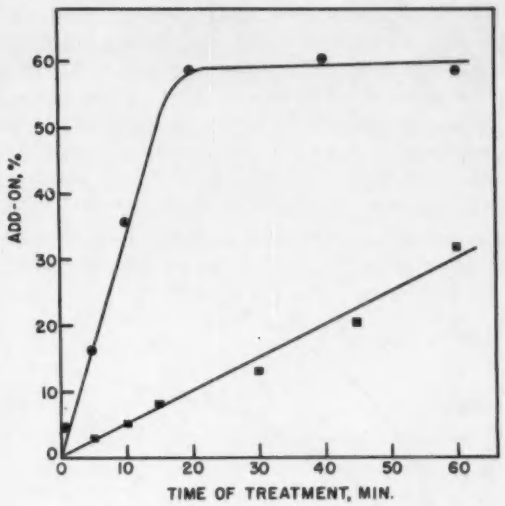


Fig. 1. The effect of treatment of partially carboxymethylated cotton, DS 0.07 (○), and mercerized cotton (□) with 10% beta-propiolactone in xylene at reflux.

This beta-propiolactone treatment saponification process with partially carboxymethylated cotton offers another method of preparing a cellulose derivative with mixed ether substituents.

Cyanoethylation with Acrylonitrile

The addition of cellulose to acrylonitrile, in a Michael-type condensation, has been studied extensively. The reaction has been adapted to cotton, and the products are considered to be of potential value [2, 6, 10].

As an extension of this work, the cyanoethylation of partially carboxymethylated cotton has been investigated. As would be expected, the extent of the reaction was greatly increased. The increased swellability of the cotton, because of the presence of carboxyl groups, should make many more hydroxyl groups available for immediate reaction. In the samples used, only a small part of the hydroxyl groups were substituted with the carboxymethyl group (DS 0.1). The increase in reactivity is shown in Figure 2, which presents the data obtained on treatment of partially carboxymethylated cotton,

mercerized cotton, and native cotton. The cloth samples were padded with 2% sodium hydroxide solution to about 80% wet pickup and treated with acrylonitrile at reflux (75° C.) for various times.

The rate and extent of the cyanoethylation was considerably greater for partially carboxymethylated cotton than for the mercerized control. The latter had been shown previously to react much faster than native cotton, as is borne out here, probably due to the greater swelling and accessibility produced by mercerization.

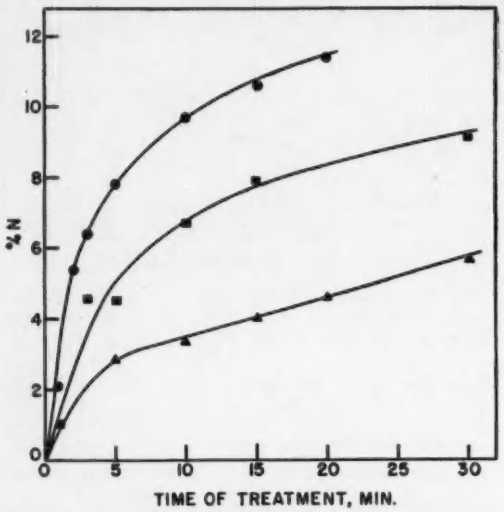


Fig. 2. The effect of treatment of partially carboxymethylated cotton, DS 0.1 (○), mercerized cotton (□), and native cotton (△) with acrylonitrile at reflux.

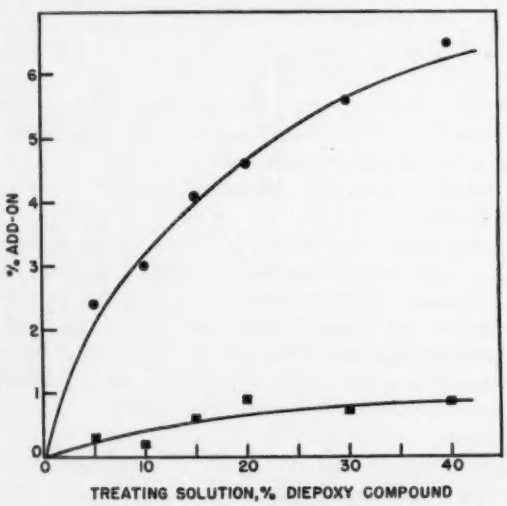


Fig. 3. The effect of treatment of partially carboxymethylated cotton, DS 0.07 (○), and mercerized cotton (□) with a diepoxy finishing agent without added catalyst.

Consideration was given to the possibility that the increased reactivity might be due to the contribution of the catalytic action of the alkalinity of the sodium carboxymethylcellulose. This was discounted because cyanoethylation of the sodium salt of carboxymethylcellulose is almost negligible in the absence of added catalyst. Another possible explanation is that there may be a hydrotropic effect of the carboxymethyl substituents. Klein and coworkers [14] have shown that certain hydrotropic salts increase the solubility of acrylonitrile in dilute aqueous alkali. The increased solubility in the water phase, which is intimately associated with the cotton cellulose during cyanoethylation, is believed to be the determining factor in both rate of reaction and the extent of cyanoethylation. Preliminary tests, however, indicated that acrylonitrile had decreased rather than increased solubility in 2% sodium hydroxide solution containing various amounts of sodium carboxymethylcellulose.

In Table III are shown the nitrogen contents introduced by cyanoethylation of three samples of partially carboxymethylated cotton yarns and a mercerized control. All four samples were treated with acrylonitrile in the same reaction flask after pretreatment with 2% sodium hydroxide solution. The greater the DS of the partially carboxymethylated cotton, the greater is the amount of swelling and, in this case, the greater the degree of cyanoethylation. It was concluded, therefore, that the increase in extent of cyanoethylation was due to the increased swelling and associated increased availability of hydroxyl groups.

TABLE III. Cyanoethylation of Partially Carboxymethylated Cotton Yarn of Various Degrees of Substitution

Yarn treated*	Nitrogen content, %
Mercerized cotton	5.3
Partially carboxymethylated cotton, DS 0.03	6.7
Partially carboxymethylated cotton, DS 0.05	7.5
Partially carboxymethylated cotton, DS 0.11	8.3

* Yarns soaked in 2% aqueous sodium hydroxide solution, centrifuged to about 80% wet pickup, and treated with acrylonitrile at reflux for 5 min.

Treatment with Epoxy Compounds

With the recent introduction of commercial diepoxy finishing agents for producing crease-resistant cottons [26], it was decided to study the reaction of epoxides with partially carboxymethylated cotton. Compounds bearing an epoxy group, or oxirane ring, are reported to react readily with carboxylic acids without the necessity of catalysis. Reaction with alcohols, on the other hand, is very slow, and a catalyst is needed.

Samples of partially carboxymethylated cotton of DS 0.1, in the free carboxyl form and of mercerized cotton, were treated with 5–40% concentrations of a diepoxy finishing agent (believed to be the 1,3-diglycidyl ether of glycerol) without added catalyst. Samples were impregnated with the epoxy compound solutions, padded to 70–75% wet pickup, mounted on pin frames, then dried at 60° C. for 7 min. and cured at 180° C. for 3 min. After a process wash with nonionic detergent, the samples were dried and the add-ons determined; these data are shown in Figure 3. Although the add-ons were much higher for carboxymethylated cotton than for the mercerized control, the efficiency of the treatment was very low. Efficiency of the sample with the highest add-on, 6.5%, was calculated from the wet pickup to be about 22%. With more dilute solutions, the efficiency was greater but the add-ons were lower.

These epoxy treated samples were tested for wrinkle resistance. As would be expected from the add-ons, the mercerized samples had practically no increased wrinkle resistance. However, the samples of partially carboxymethylated cotton had wrinkle-recovery angles of 194–235° (warp plus filling). Higher add-ons would, apparently, produce a better wrinkle-resistant finish.

The wrinkle resistance imparted by the treatment apparently indicates a cross-linkage of the cellulosic chains has occurred. Analysis of the fabric indicated that the cross-links were bound through ether rather than ester linkages. Titration of the samples showed the carboxyl content to be practically unchanged after the epoxy treatment. If reaction had taken place through the carboxymethyl groups, the carboxyl content would be diminished. Further, a test dyeing with a disperse dye introduced very little staining in the fabric. If ester linkages were formed in reaction with the diepoxy finishing agent, this test would be expected to produce more dye uptake. The indication is, therefore, that reaction of the diepoxide was primarily with the cellulosic hydroxyls rather than with the carboxyl group of the ether substituent.

Greater reaction of partially carboxymethylated cotton with another epoxy compound, ethylene oxide, has also been observed. The etherified cotton, DS 0.1, was impregnated with 2% aqueous sodium carbonate solution and then treated with a 4% solution of ethylene oxide in carbon tetrachloride for 1 hr. at gentle reflux. This sample had an add-on of 2.4%, compared with 0.6% for a sample of ordinary cotton similarly treated.

Treatment with APO

Tris(1-aziridinyl)phosphine oxide, referred to as APO, has received considerable attention at this Laboratory for the modification of cotton. Successful processes for imparting flame resistance and crease resistance based on this material have been perfected [8, 18].

The treatment of partially carboxymethylated cotton with APO was tried. Reaction through the free carboxyl groups or the cellulosic hydroxyls, or both, was considered to be possible without added catalyst.

Samples of cotton print cloth and of partially carboxymethylated cotton print cloth, DS 0.1, with the substituents in the free carboxyl form, were impregnated with 5, 10, and 20% aqueous solutions of APO without added catalyst. The samples were mounted on pin frames, dried at 80° C. for 10 min., and cured at 140° C. for 5 min. After a process

TABLE IV. Treatment of Partially Carboxymethylated Cotton with APO *

APO Solution, %	Cotton		Partially carboxymethylated cotton, DS 0.1†	
	Add-on, %	Wrinkle recovery angle, deg., W + F	Add-on, %	Wrinkle recovery angle, deg., W + F
— (Control)	—	178	—	149
5	0.7	184	2.5	151
10	1.9	194	5.7	167
20	3.5	204	12.6	214

* Samples impregnated with APO solutions, mounted on pin frames, dried at 80° C. for 10 min., cured at 140° C. for 5 min., and process washed.

† Carboxyl groups in the free acid form.

wash with nonionic detergent and air equilibration, the add-ons recorded in Table IV were determined. Reaction of the partially carboxymethylated cotton was markedly greater. The carboxyl groups of the modified cotton have apparently either provided reactive sites for attachment or catalyzed the polymerization of the APO or its reaction with the cellulosic hydroxyl groups. Although the wrinkle resistance has been improved by the treatment, the magnitude of the changes seems to indicate a limited degree of cross-linkage. It appears more likely that the APO has been mainly polymerized within and upon the fibers with only a limited amount of reaction with the fibers. APO can form a three-dimensional polymer which is extremely insoluble and resistant to removal from the fiber. The samples with the higher add-ons had a measure of flame resistance when tested by the "around the clock" test [19], but would not pass the standard vertical flame test.

Oxidation with Chromic Acid

A preliminary report on the oxidation of partially carboxymethylated cotton with chromic acid for the preparation of alkali-soluble textiles has been presented [25]. It was shown that a fibrous product with good strength retention can be produced from the etherified cotton which is completely disintegrated and almost totally soluble in hot 10% sodium hydroxide solution. With ordinary cotton, stronger oxidation conditions are necessary to obtain comparable solubility, with consequent complete loss of the valuable fibrous nature of the starting material.

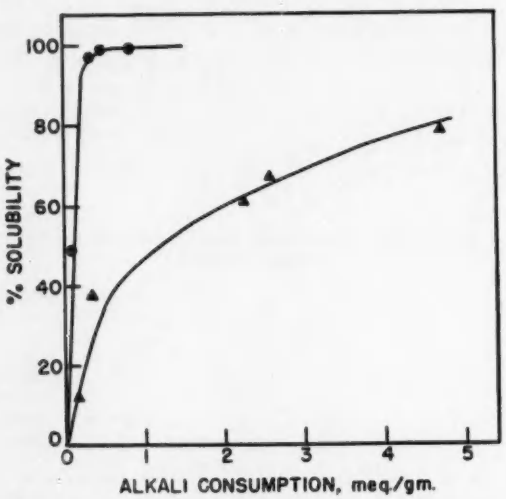


Fig. 4. Comparison of the solubility in hot 10% sodium hydroxide solution and the alkali consumption of samples of partially carboxymethylated cotton, DS 0.1 (○), with native cotton (△), both oxidized with various concentrations of chromic acid solution for 1 hr. at 25° C. The alkali consumptions of the carboxymethylated samples are corrected for the uptake due to the carboxymethyl groups.

Since the time of the original report of the process, an attempt has been made to determine the relative degrees of oxidation necessary to produce solubility. It was recognized that, because of the solubilizing effect of the carboxymethyl substituents on the fragments of the cellulose chain which are cleaved by the action of alkali on the oxidized material, the extent of oxidation necessary to produce equal solubility is substantially less for the etherified cotton than for ordinary cotton.

The action of chromic acid on cellulose is primarily an oxidation of the 2,3-dihydroxy group of the anhydroglucose units to dialdehyde groups [15]. However, the reagent is not as specific in this reaction as are those of certain other reagents, particularly periodic acid and lead tetraacetate. Because of the other reactions which accompany oxidation to dicarbonyl groups, the determination of the degree of oxidation of the cellulose with chromic acid is very complex.

A nonquantitative but somewhat analytical approach to this determination was achieved using the method of Hofreiter and coworkers [11]. These researchers have shown that the quantitative alkali consumption by periodate oxystarch and oxycellulose under standardized conditions can be used to give a rapid estimation of the dialdehyde content.

Samples of partially carboxymethylated cotton (DS 0.1) and of ordinary cotton cloth were oxidized by treatment at 25° C. with 1–14% solutions of chromic acid for 1 hr. Figure 4 presents a comparison of the solubilities of the samples in 10% sodium hydroxide solution with their alkali consumption as measured by the Hofreiter method. The alkali consumption of the oxidized-carboxymethylated cottons have been corrected for the uptake due to the acid carboxymethyl groups. Although the alkali consumption cannot be taken as an absolute determination of the degree of oxidation, it is believed that the comparison of the two curves of Figure 4 offers an indication of the relative degrees of oxidation necessary to produce comparable solubility in the two fabrics.

The practical advantage of the milder oxidation is

emphasized in Figure 5. It can be seen that it is possible to achieve 99% alkali solubility with the retention of about 65% strength on the chromic acid oxidation of partially carboxymethylated cotton. Oxidation of ordinary cotton resulted in total loss of strength with less than 80% alkali solubility.

Oxidation with Nitrogen Dioxide

Nitrogen dioxide is reported to react preferentially at the 6 carbon position of the anhydroglucose unit in cellulose, oxidizing the primary alcohol to a carboxyl group [27]. The reaction has been used to produce cotton fabrics soluble in mildly alkaline solutions. In fact, the oxidized fabric is soluble at the pH of blood, and advantage has been taken of this property to use such oxidized fabric in surgical dressings which may be left in a wound to be absorbed by the body at a later date [13]. Extreme care must be exercised to be sure that the fabric is completely soluble. It is probable that the use of nitrogen dioxide oxidized partially carboxymethylated cotton would be advantageous for surgical applications but this study has not been made as yet. It was found that under equivalent conditions of oxidation there is a clear advantage for the use of partially carboxymethylated cotton. In Figure 6 are shown the solubilities in cold 1% sodium carbonate solution of samples of cotton print cloth, carboxymethylated (DS 0.1) and mercerized, which have been oxidized with gaseous nitrogen dioxide at 25° C. for various periods of time. Under the conditions used, the mercerized samples reached a solubility of about 30% after 25 hr. of oxidation, while the carboxymethylated samples were about 94% soluble after only 4 hr. of treatment. It is interesting to note the breaks in the curves of Figure 6 which occur for both sets at 4 hr. of reaction time. The technique for the recirculation of the gas was not used, and it may be that the oxidant was essentially all consumed after this period, although the brownish-orange color of the gas was still apparent in the reaction tubes.

Strength of the carboxymethylated cotton was greater than that of the mercerized cloth after oxidation. For example, after 4 hr. of treatment with nitrogen dioxide, the carboxymethylated cotton retained 79% of its original strength; the mercerized, 55%. After 25 hr. of treatment, retentions were 68% and 48% respectively. Correlation of these strength retentions and the solubilities of Figure 6 indicate practicability of a combined partial carboxymethylation-oxidation treatment. Storage tests have not been made, but it is possible that the carboxymethylated cotton would have improved stability against the acid degradation which normally occurs in such oxidized material. An oxidation process such as this could be used to produce a fibrous textile material, soluble in mild alkaline solutions but with good mechanical strength. Many potential commercial applications of such products have been described [23].

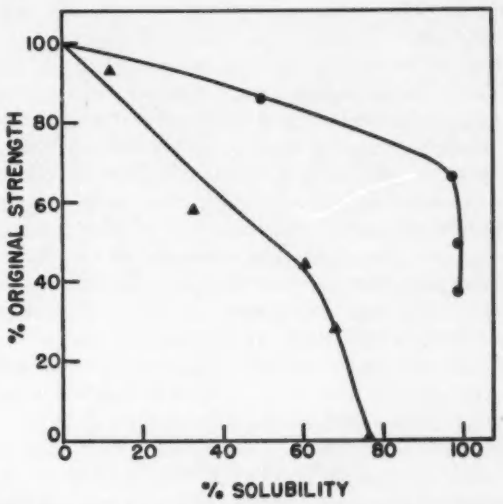


Fig. 5. Comparison of the strength retained and solubility in hot 10% sodium hydroxide solution of samples of partially carboxymethylated cotton, DS 0.1 (○), with native cotton (△), both oxidized with chromic acid.

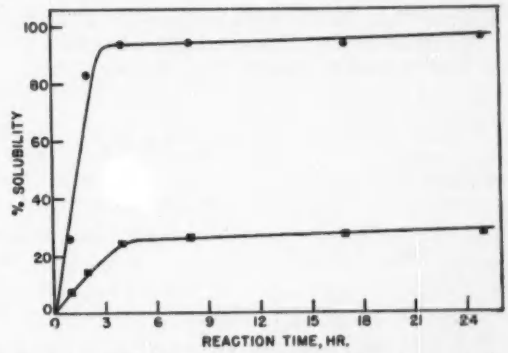


Fig. 6. Solubility in 1% sodium carbonate solution of samples of partially carboxymethylated cotton, DS 0.1 (○) and of mercerized cotton (□), both oxidized with gaseous nitrogen dioxide at 25° C.

Summary

Carboxymethylated cotton, a partially etherified cellulose derivative, has been investigated as an intermediate for further chemical modification. The etherified cotton, which retains the valuable fibrous nature of cotton, bears two functional groups—hydroxyl and carboxyl—which are capable of further reaction.

Partially carboxymethylated cotton has been treated with a number of different reagents. Textiles with bactericidal and fungistatic activity have been produced by formation of phenylmercuric and mercuric salts. Reaction with beta-propiolactone introduces carboxyethyl, hydroxypropionic acid ester, and graft polyester substituents. Addition with acrylonitrile introduces another ether substituent, the cyanoethyl group. Treatment with a diepoxy finishing agent, without added catalyst, apparently results in cross-linkage of the cellulosic chains with the production of wrinkle resistance. A degree of flame resistance was obtained by treatment with a triaziridinyl compound without catalyst. Oxidation with chromic acid or with nitrogen dioxide yields fibrous textile materials which are alkali soluble.

The rate and extent of many of these reactions were greater than those of native cotton treated under similar conditions.

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A Study of the Relationship Between Dye Absorption and Cotton Fiber Properties at Equilibrium[1]

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Abstract

The relation between cotton fiber properties and dye absorption at equilibrium has been studied for nine cotton samples representing a large range of fiber properties. The absorption was studied both for mercerized and unmercerized cotton samples. A relationship was found to exist between dye absorption at equilibrium and the Micronaire and maturity of American Upland type cotton. A linear relationship was found to exist between maturity and dye absorption at equilibrium.

The barium hydroxide absorption also was determined; similar results were obtained.

Introduction

The relationship between the structure of fibers and their dyeing properties has been the subject of many recent investigations. The effect of dye concentration, salt concentration, and temperature on dye absorption have been the subject of many experiments, beginning with the classical studies by Neale and Stringfellow [10] and Boulton and Morton [3]. Previously rate and equilibrium generally were confused.

Comparative dye studies using cuprammonium and viscose cellulose as well as mercerized cotton have been made in order to determine the effect of cellulose structure on the equilibrium absorption of dye. Hanson, Neale, and Stringfellow [8] found that the most crystalline cellulose absorbs less dye. The order of increasing dye absorption was found to be

Hydrocellulose
Cotton
Mercerized cotton
Viscose
Cuprammonium rayon

Griffiths and Neale [17] investigated the equilibrium absorption of many different dyes by viscose rayon and cotton. In all cases viscose exhibited a greater absorption than did cotton, although the ratio of absorption did not remain constant.

Furvik [5] recently investigated the dyeing properties of mature and immature cotton and found marked differences in the rate of absorption, but they reported that the amount of dye absorbed at equilibrium was constant.

X-ray diffraction studies have been made on mercerized and nonmercerized cotton as well as on mature and immature fibers by Berkley [2]. These studies showed a marked difference in the crystallinity and crystallite orientation of mature and immature fibers as well as between mercerized and nonmercerized cotton. These differences should affect the equilibrium dye absorption.

Differences in dyeing of cotton always have been known and the character of the cotton as determined by the classer's hands has been the main criterion in predicting dyeing properties. In other words, a neppy, soft and wasty cotton has been regarded as having poor dyeing properties.

During the last five years the use of cotton testing equipment has become almost universal; with these instruments the possibility of determining fiber properties on a scientific basis throughout the industry has become possible.

A major contribution to the relation of fiber properties and dyeing characteristics, differential dyeing, has been made by Goldthwait, Smith, and Barnett [6]; it has been accepted as a tentative method to determine the dyeing properties of cotton by the

[1] The study upon which this report is based has been supported by The Cotton Research Committee of Texas; The Texas Cotton Association; Anderson, Clayton, and Company, Houston; W. D. Felder Cotton Company, Dallas; Esteve Hermanos, S.A. de C.V., Matamoros, Mexico; and Esteve Brothers, Dallas.

American Society for Testing Materials [1]. The results of this test have been shown to be related to the amount of mature and immature fibers which a sample contains.

In the present investigation, attempts have been made to find out whether or not any direct relationship exists between the extent of dye absorption and cotton fiber properties, particularly Micronaire, which is related both to maturity and crystallinity of American Upland cotton. With the same object in view, the extent of absorption of barium hydroxide also was determined.

Experimental

Determination of Dye Absorption

The Beckman photoelectric spectrophotometer was used in these determinations. Two direct dyes, one with a low molecular weight and the other with a higher one, have been chosen for the present study; these are Chlorantine Fast Green BLL (Mol. wt. 1350, C.I. No. Pr. 425) and Diphenyl Fast Red 5 BL (Mol. wt. 675, C.I. No. 278). The wave lengths for maximum optical density for the green and red dyes were found to be 600 mμ and 510 mμ respectively. At these wave lengths, the optical densities of a range of dye solutions were plotted against their concentrations; for each dye a linear relationship between optical density and concentration was found. The readings for optical densities in these determinations were kept between 0.2 and 1.0 (60–10% transmittance), since readings outside this range represent solutions which are too light or too dark for the most accurate measurements. From the optical density of a solution of the dye, its concentration was calculated easily from a plot of optical density against dye concentration. Duplicate determinations were made and were found to be reproducible within 3%.

Mercerization

A cotton sample (10.0 g.) was treated with 200 ml. of 20% sodium hydroxide solution with agitation for 5 min. at room temperature, washed and decanted several times with excess water, acidified with acetic acid, and then washed and decanted several times with water until neutral to litmus.

The Dyeing Procedure

The cotton sample first was dewaxed with carbon tetrachloride in a Soxhlet apparatus, dried, and conditioned at 66% RH at room temperature by keeping it over saturated $NaNO_2$ solution in a desiccator for three days.

Dyeing in the present study was carried out with low dye and electrolyte concentrations and at boiling temperature with a refluxing condenser; the boiling temperature not only hastened dye absorption but also provided the dyebath with constant agitation.

Conditioned cotton samples (2 g.) mercerized and unmercerized were placed into a 100-ml. solution prepared from 50 ml. of 0.2% dye solution, 10 ml. of 2% sodium chloride solution, and 40 ml. of distilled water contained in a 500-ml. round-bottomed flask; the fiber–liquor ratio was 1 : 50. The contents were refluxed for 1 hr. Then an aliquot portion of the dye solution was removed, its concentration determined, and the milligrams of dye absorbed by 2 g. of cotton calculated. It should be noted in this connection that, on refluxing a dye solution for 1 hr. without cotton, there was no change in concentration

TABLE I. Varieties, Growing Areas, and Fiber Properties of the Cotton Samples Used in This Study*

Sample number	Cotton variety	Growing area	Micronaire	Maturity, %	Pressley 1000 lb./sq. in.		Elongation, %
					0 Gauge	⅛-in.	
I	Rowden	Central Texas	5.7	92	85	3.5	6.5
II	Blightmaster	Hillsboro	5.0	90	85	3.7	7.6
III	Acala 442	Mexicali	4.7	89	93	4.0	7.5
IV	DPL 15	Valley	4.4	88	84	4.0	7.8
V	TSA–DPL	Brazos	4.2	86	80	3.0	6.5
VI	Lankart	Lubbock	3.8	80	82	3.3	6.5
VII	Paymaster	Lubbock	2.9	70	74	3.5	9.9
VIII	Arizona 44	Phoenix	2.5	52	75	3.7	9.4
IX	Pima	El Paso	3.3	82	96	6.1	10.4

* The fiber properties were determined by Dr. Nell Glasscock, presently on the faculty of Alabama Polytechnic Institute.

of the solution. All of the experiments were carried out in duplicate.

Determination of Barium Hydroxide Absorption

The procedure adopted was that of Edelstein [4]. In this, 30 ml. of 0.2603 *N* barium hydroxide solution was added to 2 g. of a conditioned sample (mercerized or unmercerized) contained in a 250-ml. conical flask. The cotton sample was submerged in the solution very quickly, by means of a glass rod, and the flask was stoppered and agitated in a mechanical shaker for 2 hr. at room temperature. Then 10 ml. of the barium hydroxide solution was withdrawn and titrated with 0.11053 *N* HCl solution, using phenolphthalein as an indicator. Also, 10 ml. of the blank barium hydroxide solution was titrated. All of the experiments were done in duplicate; the mean values were expressed as milliliters of *N*/10 barium hydroxide absorbed by 2 g. of cotton. Also, the barium activity number for each mercerized sample, which is the ratio of the barium hydroxide absorbed by the mercerized sample to that absorbed by the unmercerized sample when multiplied by 100, was calculated.

Determination of the Fiber Properties

The fiber properties of the cotton samples were determined according to ASTM procedures [1]. The following tests were made.

1. Micronaire, ASTM procedure D 1448-56
2. Maturity, ASTM procedure D 1443–56
3. Strength, zero gauge, ASTM procedure D 1445–57
4. Strength, ⅛-in. gauge, ASTM procedure Appendix XIII
5. Elongation, ASTM procedure Appendix XIII

Results and Discussion

The cottons which were used in this investigation are listed in Table I. They were selected to represent a large range of fiber properties, although they do not in all cases represent the average fiber properties of their varieties.

The dye absorption at equilibrium by the nine cotton varieties selected was determined for Chlorantine Fast Green BLL and Diphenyl Fast Red 5 BL. These were the dyes used by Goldthwait in his differential dye study, as noted; they were selected because they represented a very large and a small dye molecule, respectively. The results obtained from the absorption of both of these dyes by the mercerized and the unmercerized cotton are given in Table II.

Mercerized cotton has been known to have a greater dye absorption than the unmercerized; Benzopurpurine 4B absorption has been used as a measure of mercerization, as suggested by Knecht [9]. In all cases mercerized cotton displayed a greater dye absorption than the unmercerized cotton, but the change in absorption was much greater for the cottons of greater maturity and Micronaire.

TABLE II. Absorption of Diphenyl Fast Red 5 BL and Chlorantine Fast Green BLL by Nine Cotton Samples from 100 Ml. of 0.1% Dye Solution Containing 1% Sodium Chloride at Reflux Temperature

	Mg. of dye absorbed by 2.0 g. of cotton			
	Chlorantine Fast Green		Diphenyl Fast Red	
Sample number	Raw	Mercerized	Raw	Mercerized
I	21.50	36.00	21.00	38.00
II	26.50	36.14	23.25	38.20
III	22.30	38.65	20.70	39.28
IV	27.25	38.75	24.00	38.36
V	26.00	39.75	24.00	38.75
VI	28.00	41.00	26.00	40.75
VII	35.48	43.50	32.48	43.00
VIII	46.60	47.35	43.20	47.76
IX	36.40	43.90	32.48	45.75

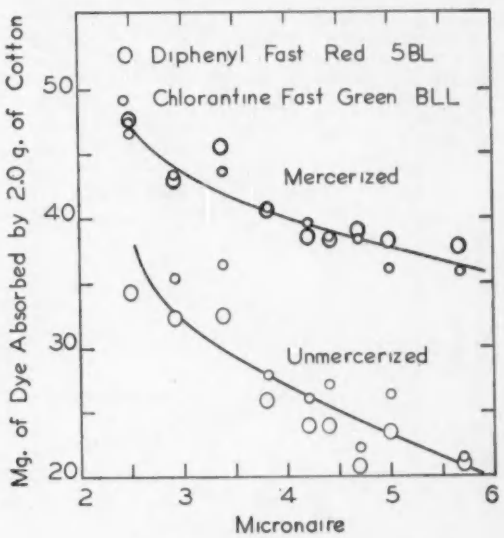

Fig. 1

The main purpose of this investigation was to determine whether or not there is a relation between the fiber properties determined, as noted. These properties included maturity, Micronaire, Pressley Index, elongation, and the dye absorbed by the cotton at equilibrium. In Figure 1, the dye absorption was plotted against the Micronaire of the cotton; a definite relation was found to exist. In Figure 2 the dye absorption was plotted against the maturity of the cotton; a linear relationship was observed. Only one cotton sample, Pima, failed to follow both of these relations. Pima cotton belongs to the extra long staple group known as *Gossypium Barbadense* L. These results indicate that factors other than maturity are involved in determining the dye absorption of cotton fibers. With the American Upland varieties this absorption was found to be related directly to maturity, since all other factors that may be involved were similar.

The results at hand are insufficient to give a definite explanation as to the anomalous behavior observed for Pima cotton, but this behavior may be related to the high elongation observed for this variety; elongation was found by Berkley to be related directly to crystallite orientation. The barium hydroxide absorption by mercerized and unmercerized cotton was determined for comparative purposes; these results are given in Table III. There was found to be a relation similar to that observed for dye absorption between barium hydroxide absorption and barium hydroxide activity number and

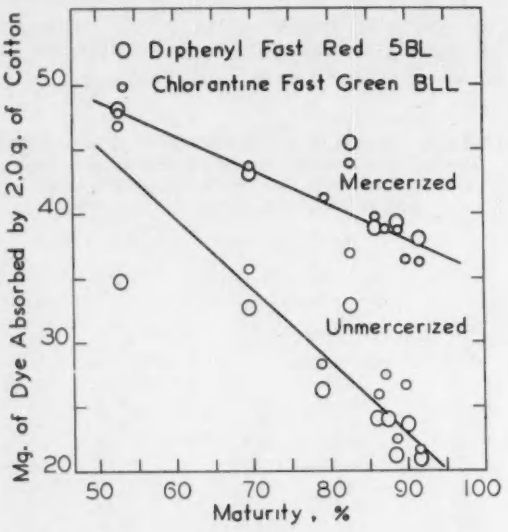

Fig. 2

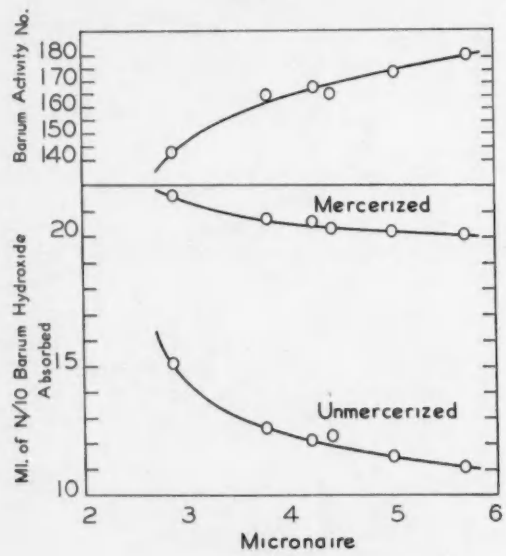

Fig. 3

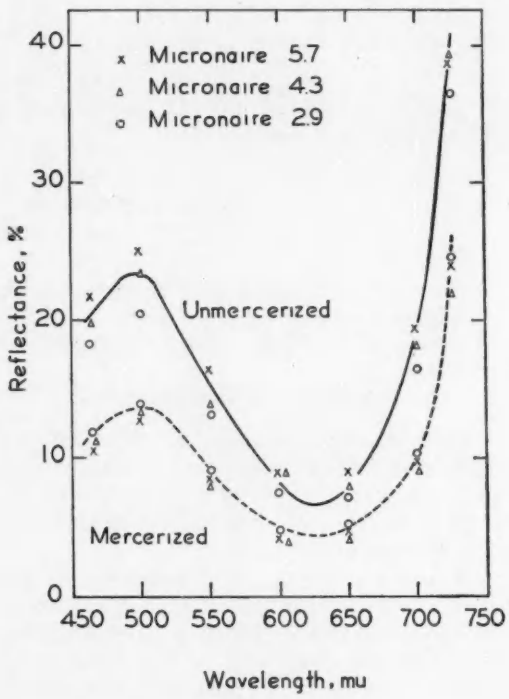

Fig. 4

Micronaire and maturity. The relation obtained for Micronaire is plotted in Figure 3.

The relation obtained between dye absorption and barium hydroxide absorption makes these determinations a possible method for the evaluation of the maturity of American Upland cotton.

The greater absorption of dye by less mature fibers is in accord with previous investigations, which reported that the immature or fine cotton had a lower crystallinity and therefore was more amorphous, displaying a greater accessibility.

The fact that absorption was correlated both with Micronaire and maturity was to be expected, since there is a fairly good relation between the fineness and maturity of Upland cottons.

The effect of Micronaire on the color of the fibers dyed to equilibrium was not noticeable. The same results were obtained for the unmercerized and mercerized fibers, respectively. The mercerized fiber dyed a darker shade. In Figure 4, the light reflectance as measured by the spectrophotometer is plotted for fibers of three different Micronaire values. It should be noted, however, that dyeing to equilibrium will give results which are different from those obtained in commercial dyeing, either of yarn or fabric, since equilibrium is only one of the many factors involved. In future reports the effect of fiber properties on the rate of absorption and desorption of cotton fibers will be studied, as well as the dyeing of cotton yarns and fabrics, in an effort to determine further relationships between fiber properties and dyeing.

TABLE III. Barium Hydroxide Absorption and Barium Activity Number for Six Cotton Samples Having Different Fiber Properties

Sample number	Vol. of $N/10$ $Ba(OH)_2$ absorbed by 2 g. cotton, ml.		Barium activity number
	Raw	Mercerized	
I	11.10	20.05	180.6
II	11.60	20.25	174.2
IV	12.25	20.35	165.7
V	12.20	20.55	168.5
VI	12.55	20.70	165.4
VII	15.10	21.55	142.8

Acknowledgments

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Stress-Strain Response of Fabrics Under Two-Dimensional Loading

Part I: The FRL Biaxial Tester

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Abstract

The general philosophy of biaxial testing is discussed and several criteria established for the performance of such tests. Existing testers have been evaluated in the light of these criteria and shortcomings pointed out. A tester developed in 1952 and embodying the more important principles is described, and some selected results are presented to indicate the possible scope of operation. Subsequent publications will be concerned with analysis of data on mechanical fabrics.

Introduction

The tensile testing of fabric is in general primarily concerned with the load–elongation characteristics of a specimen measured in a single direction for any given test. Tests may of course be performed in more than one fabric direction, most commonly in warp and filling directions, but each is evaluated without respect to any phenomena along any axis other than that of the test. Such tests are commonly classified as "uniaxial." That such a title is a misnomer can easily be seen by observing a simple tensile test and noting the necking that takes place in the unrestrained region; deformations are therefore occurring along more than one axial direction. What is really meant by a uniaxial test is not that loads or deformations take place along only one axis, but that they are *applied* and *measured* along only one axis.

For many purposes a uniaxial test is adequate; it is an index of relative strength, of the degradation or improvement afforded by a treatment to a certain degree of extensibility, etc. Nonetheless, the practical applications of fabrics only rarely impose a truly uniaxial stress; some examples of this are tapes and belts used for power transfer in machinery and suspension lines in parachutes. In the more common cases stresses are simultaneously imposed in more than one direction; obvious examples of this are the deformations at the knee or elbow of a garment, the canopy of a parachute, and the walls of a fire hose.

The question naturally arises as to what additional information could be obtained from a test which controlled and measured more variables than does the uniaxial test, and just what form this control and measurement should take. Since most cases of interest in textiles involve plane stress (no external forces present in the depth direction), the controls and the measurements considered here will be confined to the plane of the fabric. This means that changes in the third or thickness dimension of the fabric are not explicitly considered, not that the results are inapplicable to very general types of fabric deformation as, for example, an inflated balloon. While such three-dimensional deformations are among the controlling factors in producing stress patterns, the stresses themselves may be considered to act in the "plane" of the fabric or, in terms familiar to the stress-analyst, to be membrane type stresses. Additionally, since most fabrics possess only two principal directions and most stress applications can be geometrically resolved into two orthogonal components, a pair of axes at right angles will be considered. Such tests, where loads or strains are applied simultaneously along two axes, are usually called "biaxial."

While it is not possible to assay completely the added value of biaxial over uniaxial testing, it is certainly obvious that any service function which is sensitive to fabric distortion will be better characterized by the biaxial response parameters. A good example of this is the air permeability of a parachute fabric while under load.

The idea of biaxial testing is by no means new, but all previously published work along these lines has consisted either of discrete dead loadings along different axes or of other loading programs which violate certain essentials of a test whose results are to be used as a comparative measure against the results of similar tests on other materials.

A considerable amount of work was performed at these laboratories using some simple types of two-directional straining. The results of this work showed conclusively that some other means had to be adopted if meaningful, reproducible results were to be obtained. Accordingly, the theoretical aspects of biaxial behavior were carefully investigated and a tester designed to fulfill the theoretical needs so found.

A brief inquiry into the variables involved and their influence will lead into the design criteria of the tester to be described below.

Design Criteria

Consider any biaxial testing apparatus in which pairs of grips are placed at right angles, as in Figure 1. In order to maintain a nonskewed fabric configuration during the test, it is necessary that, referred to the initial center of the test specimen, $X_1 = X_2$ and $Y_1 = Y_2$ at any time during the test. This is the first requirement of any such tester; the subscripts will therefore be dropped in the subsequent analysis. There still remain a number of variables, not all independent, required to fully describe a biaxial test and its results; these are listed in Table I.

The reason the e's, representing fabric biaxial strains, cannot be inferred from the L's, representing grip separations, is that true biaxial strain exists only in a region between both sets of jaws and sufficiently far from each such that the boundary effect of clamping is no longer perceptible. Near the grips the specimen is under uniaxial stress; near the center, under controlled biaxial stress; and between lies a transition region in which stresses and strains are complicated functions of both grip separation and fabric properties. Clearly, it is not possible to state the biaxial strains from a knowledge of the grip separation alone. Thus the second requirement of a biaxial tester can be formulated; strains must be measured within the controlled biaxially stressed region of the specimen.

TABLE I. Variables in a Biaxial Test

N_x, N_y	loads per unit width in the X and Y directions
e_x, e_y	biaxial strains (strains in the region free from boundary effects of grip attachment)
L_x, L_y	grip separation in the X and Y directions
$\frac{dN_x}{d_t}$, $\frac{dN_y}{d_t}$	rate of change of the above quantities with respect to time
$\frac{de_x}{d_t}$, $\frac{de_y}{d_t}$	
$\frac{dL_x}{d_t}$, $\frac{dL_y}{d_t}$	

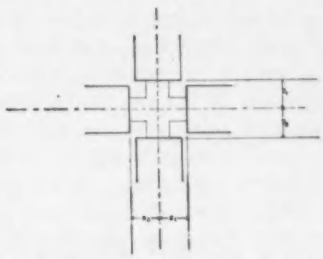

Fig. 1. Gripping jaw configuration in a biaxial test.

The next item to consider is load or extension programming. In a uniaxial test the controllable variables are load and extension. Commonly, although not always, the rate of change of one of these is held constant, resulting in a constant rate of load or constant rate of extension machine. The two variables are, of course, not independent; either having been programmed, the other is fixed by fabric parameters. In a biaxial test the situation is considerably more complicated due to the increased number of variables and the orthogonal interaction between the yarn systems. The load–elongation relationships for such a test can be given by the two differential equations.

$$de_x = \frac{1}{E_x} dN_x - \nu_{xy} \frac{1}{E_y} dN_y$$

$$de_y = \frac{1}{E_y} dN_y - \nu_{yx} \frac{1}{E_x} dN_x$$

The ν's are analogous to Poisson ratios in that they reflect the influence of strain along one axis on strain along another, but they are neither constant nor linear. Likewise E_x and E_y, the X and Y tensile moduli, are neither constant nor linear but depend in a complicated way on fabric and yarn parameters and the previous loading history. Clearly then, the principles of superposition do not apply and

the above equations cannot be solved in any practical form. Also, since the interrelationship of fiber, yarn, fabric, and test parameters is unknown, quantitative comparison of test results demands that the same sequence of test events be applied in each case. As a corollary it can be stated that no amount of uniaxial testing, regardless of the manner or number of directions in which such testing is performed, can be used to quantitatively predict biaxial performance. A little thought will show that the programming must consist of the simultaneous specification of either both loads or both extensions in the controlled stress region. In the present case the loads were chosen as the independent variables for three reasons: they are easier to work with in cloth geometry theory; they are easier to control in a biaxial test, a purely practical consideration; and for the material of paramount interest at the time of design, airship envelope fabric, the loads were the independent variables in the end use.

By neglecting the role of rate of loading, a subject to which further reference will be made later,

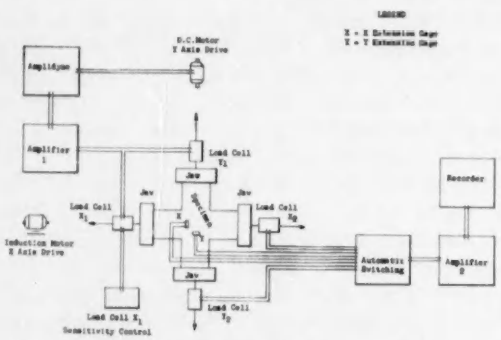

Fig. 2. Block diagram of biaxial tensile tester.

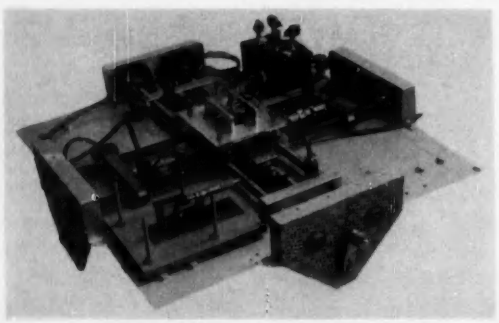

Fig. 3. Mechanical portion of tester with extension-measuring devices in position.

the biaxial test can be considered completely controlled and reproducible by the control of the single factor N_y/N_x which, since square samples were used throughout, is the ratio of loads in the two directions. It is this type of control which was adopted, and this ratio will subsequently be referred to as K.

In summary, the following specifications are necessary for biaxial tensile testing.

1. Straining must be such that a controlled biaxially strained region exists at the specimen center.
2. Strains must be measured in this region.
3. The ratio of loads in the X and Y directions, N_y/N_x or K, must be held constant at some predetermined value during a test. This is the characterizing parameter of the test.

Of the multidirectional testers already described in the literature, only two were specifically designed for and are readily applicable to the laboratory testing of fabrics. These are those of Reichardt, Woo, and Montgomery [2] and Checkland, Bull, and Bakker [1]. Each satisfies Conditions 1 and 2 above, but since for both cases both sets of grips move at constant speed during a test, Condition 3 is violated. That is, it is the machine extensions which are controlled, while in the central region neither loads, the arbitrarily selected variable of Condition 3, nor extensions, an acceptable alternate choice, are controlled. Thus, while general trends in biaxial behavior can be determined from such machines, considerable generality is lost and quantitative comparison of different materials is not valid.

The machine described below embodies all three of the foregoing requirements.

Design of the FRL Biaxial Tester

Two orthogonal sets of jaws (Figure 1) grasp a cruciform specimen of 2-in. tail width. Opposing jaws move with equal speed. This satisfies Condition 1 and assures that there will be no skewing imposed. One set of grips, moving along a line designated as the X direction, moves at constant speed, while the other set moves at the speed and in the direction required to keep the load ratio K constant; this satisfies Condition 3. Devices are mounted over the uniformly strained region (surrounding the geometric center of the specimen) which measure the extension along both axes, e_x and e_y, thus satisfying Condition 2. The values N_x, N_y, e_x, and e_y are recorded by a single pen recorder in broken line fashion.

The mechanics of operation can be understood by referring to Figure 2, which illustrates the over-all mechanism in block form. Load cells X_1, X_2, Y_1, and Y_2 are identical and consist of electric resistance strain gauge Wheatstone bridges bonded on thin-walled Dural cylinders. These cylinders are flexibly connected to both the grips and pulling bars so that no bending or torque components can obscure the tensile deformation of the cylinders. Two of these gauges, X_2 and Y_2, are used to measure the loads in the X and Y directions while the other two, X_1 and Y_1, control the load ratio K. This is accomplished by connecting the electrical outputs of these two gauges in series opposing and using the resultant or error signal to control the Y axis drive. Thus, if the characteristics of X_1 and Y_1 are identical and N_y does not equal N_x, an error signal appears and is amplified by Amplifier 1, a Sanborn Strain Gauge Amplifier, then fed into an Amplidyne whose output runs the Y axis D.C. motor drive in whatever direction is required to re-establish this load balance. The load cell sensitivity control serves to change the ratio K by decreasing the output per unit load of the Y_1 cell.

Extension cells X and Y consist of Schaevitz Linear Differential Transformers whose motion is controlled by suitably pivoted pairs of pins. Each pair of pins lightly punctures the fabric with an initial point separation of $\frac{1}{2}$ in. straddling the specimen center. As the fabric extends or contracts, the points move and the corresponding electrical change is used as a measure of extension. The force required to move the pins is sensibly zero so that the test is essentially unaffected by their presence. It has been found experimentally that for most materials there is a region of about 1 in. square free from boundary effects so that the $\frac{1}{2}$-in. pin separation is conservative. Figure 3 shows a photograph of the device in position on a specimen.

All recording is done by a Brown Strip Chart Recorder. It receives signals via a motorized selector switch and a Sanborn Strain Gauge Amplifier, Amplifier 2. This switch connects each of the signals N_x, N_y, e_x, and e_y to the amplifier in cyclic fashion, the duration of each being about 1 sec. Provision is also made for manual selection of any of these.

Examples

Figures 4–8 give some examples of the type of information obtained from biaxial tests and have

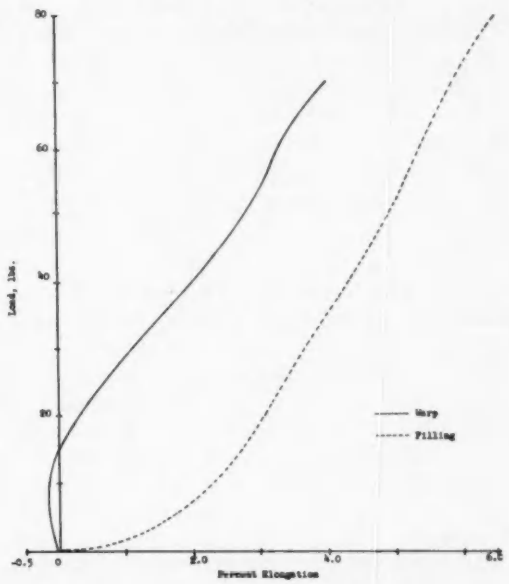

Fig. 4. Biaxial load–strain response for a cotton fabric at a warp–filling load ratio of 0.76.

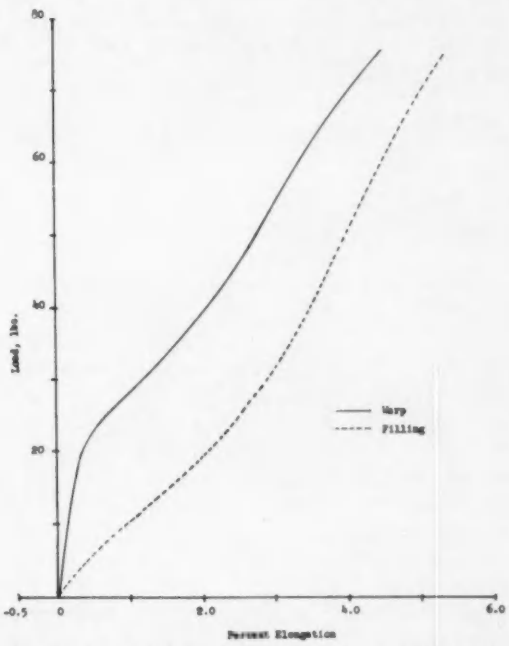

Fig. 5. Biaxial load–strain response for a cotton fabric at a warp–filling ratio of 0.86.

been chosen to illustrate particular features. Figures 4–7 show the load–elongation characteristics for a cotton fabric (used as a base for coated airship envelope fabric) at warp-to-filling load ratios, K, varying from 0.76 to 1.20. The specimen tail widths are initially 2 in. Note that for a ratio of 0.76 the shape of the warp curve is not only very steep but is actually negative near the beginning; that is, it was necessary that the warp direction contract in order to maintain the given load ratio. As the ratio progresses from 0.76 to 1.2, the warp and filling curves approach each other and pass, the 0.76 and 1.2 diagrams being quite similar but with warp and filling interchanged.

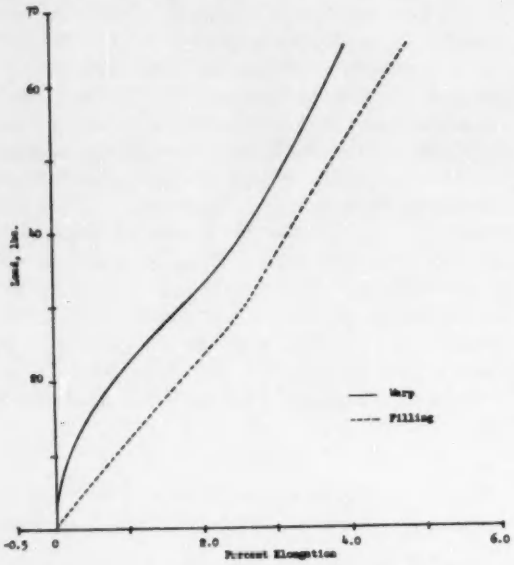

Fig. 6. Biaxial load–strain response for a cotton fabric at a warp–filling load ratio of 1.00.

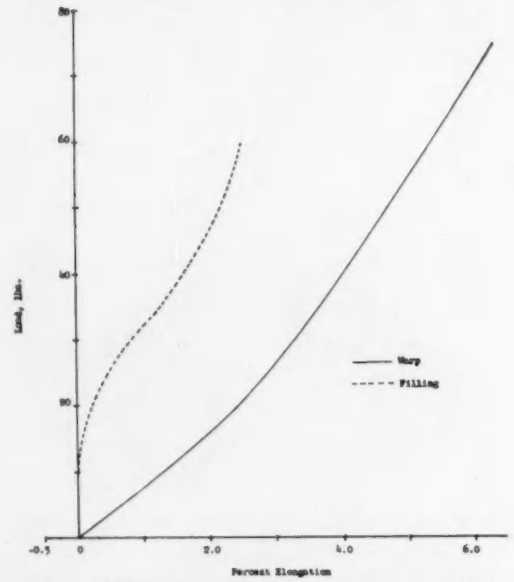

Fig. 7. Biaxial load–strain response for a cotton fabric at a warp–filling load ratio of 1.20.

Figure 8 shows the stress–strain relationships both uniaxially and biaxially at a 1:1 load ratio for a typical personnel type parachute fabric. Note that for a given load the extensions are much smaller for the biaxial case. This is very significant, since fabric permeability may depend strongly on its biaxial deformation under a pressure load.

No comment can be made here as to whether a given set of curves represents good or bad performance; this obviously will depend on the end use. However, it is quite clear from the very different response at different load ratios that an uncontrolled biaxial test wherein the load ratios can vary considerably during the test could lead to results whose meaning would be difficult to interpret.

Rate of Loading

An insufficient amount of work has been done to make any quantitative conclusions on the effects of rate of loading on biaxial tests, but clearly this may be of considerable importance with some materials. It is probably safe to say that if a material shows an appreciable rate-of-load effect in uniaxial tension, the effect will be greater biaxially. Such control is a straightforward refinement of the machine

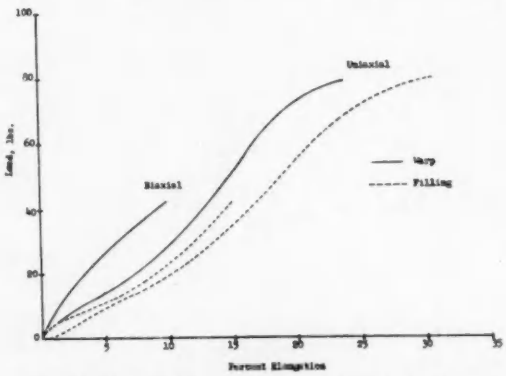

Fig. 8. Comparison of biaxial and uniaxial load–elongation with biaxial warp and filling loads equal.

described and will be accomplished if found necessary.

Acknowledgment

The author wishes to acknowledge the work of C. L. Cummings in the original design and construction of the mechanical portion of the tester and the contribution of the following individuals whose earlier work elicited the need for such a machine and aided in the definition of its functional requirements: W. J. Hamburger, M. M. Platt, and C. C. Chu.

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Use of Trifluoroacetic Anhydride in Partial Acetylation of Cotton Cellulose

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Abstract

Trifluoroacetic anhydride (TFAA) has been found to be an effective esterification promoter in the preparation of experimental quantities of partial cellulose acetates in which the fibrous structure of the original cotton is retained. In this reaction TFAA acts as an impellent and no additional catalyst is required. A method of preparation has been devised, and the effects of time, temperature, and molar ratio of the components in the reaction system have been studied. Optimum reaction conditions are mild with no great degradative effects. Cotton in the form of yarn has been reacted, and the composition and physical characteristics of the modified yarns have been determined.

Introduction

For many years, researchers at this laboratory have been interested in the partial esterification of cotton cellulose with retention of the excellent textile characteristics of cotton. Any new and promising method of esterification which accomplishes this is examined even though the current cost of the method is high.

Trifluoroacetic acid is relatively new. Since its discovery by Swarts in 1922 [10] it has not been readily available until recently, and not many references have been made to its use as an esterification catalyst for cellulose [11]. The "impelling" action of chloroacetic acids and their anhydrides on the esterification of cellulose by other organic acids has been described by Clarke and Malm [4] in numerous patents. Their reaction, however, requires the use of an additional catalyst. Trifluoroacetic anhydride acts as a catalyst, promoting the esterification of alcohols with a carboxylic acid without the introduction of trifluoroacetyl groups and without the use of any other catalyst.

Bourne et al. [1] have described the esterification of various alcohols with carboxylic acids in the presence of relatively large amounts of trifluoroacetic anhydride. In their experiments an anhydride:alcohol ratio greater than one was necessary to give good yields of the ester. This reaction proceeds under mild conditions, and it was speculated that the reaction depended upon the formation of unsymmetrical acid anhydrides. Morgan [8, 9] confirmed the formation of unsymmetrical anhydride in the esterification of cellulose to form the unhalogenated ester. Morgan was also able to esterify highly activated cellulose and polyvinyl alcohol using only

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catalytic amounts of the trifluoroacetic acid. In the absence of a second carboxylic acid, Morgan esterified polyvinyl alcohol with trifluoroacetic acid, yielding the trifluoroacetate ester; these esters lacked hydrolytic stability.

Morgan states that the chief advantage of the use of trifluoroacetic acid or anhydride as esterification catalysts is the relative ease of complete removal of the catalyst from the reaction product, requiring only a simple washing procedure in the case of cellulose. The products, washed only with distilled water, were thermally stable and did not show any appreciable cleavage of acetyl groups after four years of normal laboratory storage.

In this laboratory much work has been done on the partial acetylation [2, 3, 5] of cotton cellulose with the retention of its fibrous form. Emphasis has been on the production of a yarn having excellent heat and rot resistance. The use of trifluoroacetic anhydride as an esterification impellent for cellulose has not been thoroughly investigated, and the work reported here is intended to describe the conditions for the reaction in the partial acetylation of cotton cellulose with retention of the fibrous properties of the cotton.

Description of Apparatus

In the course of the work involving the use of trifluoroacetic anhydride in various reaction mixtures, the problem of retaining this material in the reaction vessel was encountered. Because of its high volatility (b.p. 40° C.) and a pronounced tendency to "creep," ordinary standard taper ground glass joint apparatus was found unsuitable; there was no convenient way to apply pressure and the ground glass surfaces stuck together. Stainless steel equipment was unsuited because of the corrosive nature of this anhydride. Teflon [2] lined screw capped glass containers with flat ground lips were fabricated and found inadequate in many instances because varying pressures were applied in screwing down the caps. It was then found that all-glass enclosures could be made, using the common spherical joint, lubricated with Dow Corning [2] high vacuum grease. No leakage was encountered with this reaction chamber under repeated agitation or tumbling end-over-end continuously for several days.

[2] The mention of trade names does not imply that they are recommended or endorsed by the Department of Agriculture over similar products of other companies not mentioned. Trade names are used here for convenience in reference only.

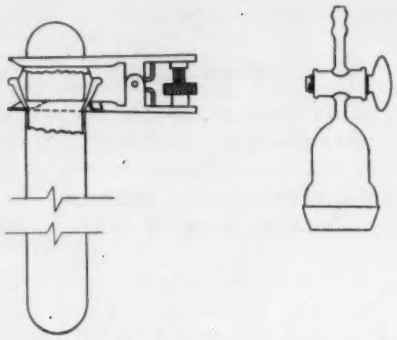

Fig. 1. Reaction chamber with top and clamp in place; alternative top with a stopcock at right.

A spherical joint of appropriate size was fused to a glass chamber of desired shape and suitable size. An appropriate clamp for the spherical joint was used and tightened to retain the joint in place and to maintain the system either under partial vacuum or pressure. A stopcock fused to the top of the stopper facilitates its use at other than atmospheric pressure. Chambers of various sizes (100–1200 ml. capacity) were fabricated. The stoppers both with and without stopcock fused to the top could be used interchangeably. A typical chamber with stoppers is illustrated schematically in Figure 1.

Experimental Procedure

Scoured 12/3 cotton yarn was selected as the experimental material to be acetylated because of the ease of handling in small skein form. The resulting products could be readily evaluated for breaking strength and acetyl content, and other information could be easily obtained on reasonably small amounts of material. In most experiments benzene was used as the diluent. The reaction was carried out by placing the weighed skeins in the above-described all-glass tubes, adding the reaction mixture, and tumbling the tubes end-over-end (about twice per minute) on a rotating wheel. After the reaction, the samples were washed in benzene, alcohol, and water, and in most cases an additional wash in dilute aqueous sodium bicarbonate was added to neutralize any possible trifluoroacetic acid remaining on the cellulose.

In Table I, the effect of the molar ratio of the reactants upon the degree of acetylation and yarn breaking strength is shown. The molar ratios represent the ratio of cellulosic OH : trifluoroacetic

anhydride : acetic acid. In these experiments the cotton consisted of 5-g. skeins of 12/3 air-dry scoured yarn receiving no prior activation. Benzene was used as the diluent (20 ml./g. of cotton). The samples were reacted by tumbling end-over-end for 24 hr. at room temperature in the all-glass reaction chambers, and the samples were subsequently washed in dilute $NaHCO_3$ to neutralize any unreacted acid left in the yarn. The optimum ratio for the reactants appears to lie between 3 : 2 : 1 and 3 : 2 : 2, in which range adequate acetylation with high efficiency was obtained with best retention of the yarn properties. It should be noted that increasing the amount of acetic acid over that of the trifluoroacetic anhydride greatly reduced the effectiveness of the TFAA as the acetylation impeller. The highest efficiency occurred when the amount of the anhydride is somewhat greater than that of the acid. The same reactions under refluxing conditions resulted in great losses in strength, as seen in Table II. A sample of yarn treated with TFAA alone in benzene diluent at reflux temperature lost all measurable strength and had no acetyl content.

The effect of activation of the cellulose on the acetylation is shown in Table III. In these experiments the skeins of yarn were variously activated and then reacted simultaneously in the same reaction chamber, each sample competing for the reactants, which were present in a 3 : 2 : 1 ratio. The reaction at room temperature proceeded for 24 hr. with continuous tumbling. The highest acetylation was obtained in the sample which had been activated by soaking in water under vacuum and the water removed by solvent interchange through alcohol into benzene. Allowing a water-activated sample simply to air-dry by coming to room equilibrium in moisture from the wet side was also quite effective. Drying through azeotropic distillation with benzene greatly reduced the effectiveness of the activation. The oven-dried sample, as would be expected, was the least reactive of this series.

The degree and uniformity of the acetylation was determined with a dye test, the mixed acetate yellow and direct cotton blue [4]. These results had a direct correlation with the acetyl values indicated.

If the variously activated yarns are reacted individually in separate reaction chambers, the results are not so variant after 24 hr. of reaction. The acetyl values are approximately the same, about 18–20% for a 3 : 2 : 1 ratio of reactants.

In Table IV is compared the acetylation of yarns brought to room equilibrium in moisture from the oven-dry side and from the wet side. The water-activated air-dried sample had the highest acetyl content and the best breaking strength retention.

A study of the effect of dilution on the acetylation reaction revealed that the diluent : cellulose ratio of between 15–25 ml./g. of cotton gave products with optimum substitution and with best textile properties.

The diluents most applicable were the aliphatic and aromatic hydrocarbons and halogenated hydro-

TABLE I. Effect of Molar Ratio of Reactants

Molar ratio*	Acetyl, %	Breaking strength retention, %
3:1:1	7.9	93.0
3:1:2	2.5	104.0
3:1:3	1.2	113.6
3:2:1	22.2	118.6
3:2:2	26.8	120.0
3:2:3	19.0	101.0
3:3:2	35.8	70.0 (stiff)
3:3:3	34.8	99.8 (stiff)
3:3:4	29.3	124.0 (stiff)
3:4:3	41.0	Brittle

* Ratio of cellulose OH : TFAA : HOAc.

TABLE II. Effect of Refluxing

Molar ratio*	Reflux time, hrs.	Acetyl, %	Breaking strength retention, %
3:1:1	1	2.4	71
3:1:1	4	4.8	46
3:1:2	1	1.0	87
3:2:0	2	0	0
3:2:1	1	19.0	60
3:2:2	1	19.0	69
3:2:2	2	22.0	55

* Ratio of cellulose OH : TFAA : HOAc.

TABLE III. Effect of Activation

Activation	Acetyl, %	Dye*
Air-dry, scoured (ADS)	9.8	yellow-green
Water under vac, air-dried	21.9	yellow
Water under vac, solvent-dried	23.6	yellow
Water under vac, Bz azeotrope-dried	12.3	yellow-green
ADS, benzene azeotrope-dried	7.0	uneven-green
Oven-dried (105° C. 4 hr.)	2.5	blue

* Mixed dye bath of acetate yellow and direct cotton blue.

carbons. It was found that esters, ketones, and ethers were not effective as diluents, due to side reactions, as reported by Hauptschein and Grosse [7].

The results of a study of the effect of time on the course of the acetylation are shown in Table V. The samples consisted of 12/3 yarn, water-activated and dried by azeotropic distillation with benzene. These were reacted in a medium containing the 3:2:2 molar ratio of the reactants, 25 ml. benzene per gram of cotton as the diluent, and tumbled at room temperature. There is a progressive increase in acetyl content up to the 24-hr. reaction period.

TABLE IV. Effect of Activation

Activation	Ratio	Acetyl, %	Breaking strength retention, %
Oven-dried, room equilibrated	3:2:2	26.5	96.5
Air-dried, scoured	3:2:2	26.8	120.0
H_2O boiled 30 min., dried to room equilibrium	3:2:2	27.3	134.0

TABLE V. Effect of Time

Sample	Time, hr.	Acetyl, %	Fluidity, Rhes	Breaking strength retention, %
Scoured control	—	—	2.5	100
Activated control	—	—	7.0	82
TFAA control	24	0.0	17.0	61
TFAA–HOAc	2	8.2	8.8	95
TFAA–HOAc	4	13.4	10.5	88
TFAA–HOAc	6	19.4	11.4	88
TFAA–HOAc	8	22.3	12.4	95
TFAA–HOAc	16	27.1	12.4	93
TFAA–HOAc	24	27.7	11.3	91

TABLE VI. Effect of Time

Time, hr.	Acetyl, %	Breaking strength retention, %
0.5	4.8	133.6
1.0	6.8	125.0
2.0	9.4	123.6
4.0	13.5	119.0
8.0	17.9	114.0
16.0	24.2	116.5
24.0	27.3	134.0
48.0	26.4	108.0

Conditions: Tumbled at room temperature, 20 ml. benzene/g. cotton. Water-activated (boiled 30 minutes) 12/3 yarn, air-dried overnight. $NaHCO_3$ neutralization. Molar ratio 3:2:2.

The fluidity values also show a slight increase, but they are not quite as high as that for the TFAA control. The breaking strength retentions were quite good for these samples, which were not neutralized but only water washed.

In another series of experiments, Table VI, samples were water-activated and air-dried overnight. After acetylation, a sodium bicarbonate neutralization treatment was used to remove any residual TFA acid. The acetyl values closely followed the values in Table V, indicating little difference due to method of activation. Breaking strength was much improved, showing that this method of activation and subsequent neutralization results in a superior product.

It is generally accepted that the mechanism for the acetylation is through the formation of an unsymmetrical anhydride from the TFAA and the acetic acid, as indicated in Formula 1 in Figure 2. If this is correct, it can be assumed that the addition of trifluoroacetic acid to acetic anhydride should also result in the formation of some unsymmetrical anhydride, as shown in Formula 2 in Figure 2. Such a system should also result in the acetylation of cellulose. Results from Table VII show that only a little acetylation was obtained when using a catalytic amount of TFA and Ac_2O; however, a somewhat higher degree of acetylation was achieved by using TFA in equimolar amount with acetic anhydride as the acetylating agent. In the presence of $Mg(ClO_4)_2$ a significantly greater degree of acetylation occurred, but not as great as that obtained

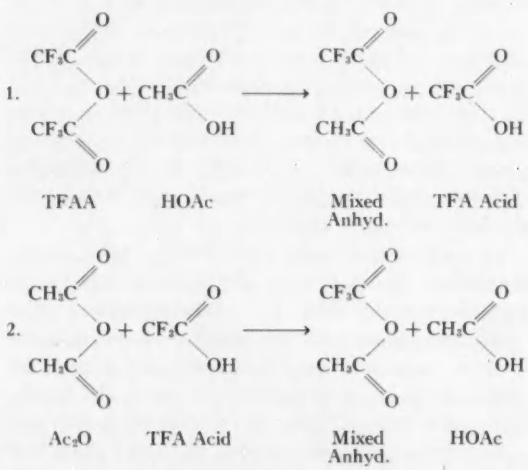

Fig. 2. Reaction mechanisms.

with equimolar quantities of TFAA and HOAc. Thus $Mg(ClO_4)_2$ appears to cause the shifting of the equilibrium in favor of the formation of the unsymmetrical anhydride from Ac_2O and TFA. The same quantity of $Mg(ClO_4)_2$ did not promote the acetylation of cellulose with Ac_2O, whereas the same amount of $HClO_4$ caused an appreciable degree of acetylation using benzene as the diluent.

A comparison of the effectiveness of TFAA and chloroacetic anhydride as impellents in the esterification of cellulose was made; in Table VIII are found the results. Chloroacetic anhydride impelled the esterification of the yarn with acetic acid in the first experiment, in which the reaction product went into solution forming a dope. In this case both the acetic acid and chloroacetic anhydride were present in great excess. In later experiments, in which benzene was used as the diluent and the acetic acid and chloroacetic anhydride were present in the same concentration and molar ratios (3:2:2) as in the examples with TFAA, no appreciable acetylation was obtained either with or without added catalyst, $\{Mg(ClO_4)_2\}$, or under reflux conditions for 2 hr., or at room temperature tumbling for 24 hr.

Summary

The acetylation of cotton cellulose has been accomplished with high efficiency with little need of a large excess of reagents. For a partial acetylation with retention of the fibrous form of cotton, it is sufficient to have only the stoichiometric quantity of the acid in the reacting solution for the degree of substitution desired. On a molar basis the amount of the impellent (TFAA) required is only slightly in excess of the quantity of the acid. This has also been found generally true for acids other than acetic [6]. The reaction conditions are mild, with no great degradative effects. In general, samples neutralized with aqueous bicarbonate had a higher breaking strength retention than those not so neutralized.

Acknowledgments

The authors wish to thank Mrs. Constance Fleming Cashen for the acetyl determinations, Miss Gloria

TABLE VII. Effect of Varying Catalyst

Code no.	Molar ratio of reactants*						Diluent†	Acetyl, %
	TFAA	TFA	Ac_2O	HOAc	$HClO_4$	$Mg(ClO_4)_2$		
1	2			2			Benzene	26.8
2	2						HOAc	0.9
3		2	2				Benzene	7.3
4		2	2			.05	Benzene	21.6
5			2			.05	Benzene	0.9
6		.05	2				Benzene	1.6
7		.05	2				HOAc	0.3
8			2		.005		Benzene	17.9
9			2		.05		Benzene	23.3
10			2		.05		HOAc	2.8

* Molar ratio of catalysts and acetylating agents based on cellulose OH=3.
† Diluent present approximately 20 ml./g. cellulose.
Conditions: Samples consisted of 5-g. skeins of 12/3 cotton yarn, water-activated and dried by solvent exchange into benzene, tumbled 24 hr. at room temperature.

TABLE VIII. TFAA vs. Chloroacetic Anhydride as Impellents

Conditions	HOAc, ml.	$(ClAc)_2O$, g.	$Mg(ClO_4)_2$, g.	TFAA, ml.	Benzene, ml.	Acetyl, %
3 hr.—60° C.	25.0	30.0	0.05	—	—	42.5*
Reflux 2 hr.	3.6	10.5	—	—	100	0.2
Tumble 24 hr.	3.6	10.5	—	—	100	0.2
Reflux 2 hr.	3.6	10.5	0.05	—	100	3.5
Tumble 24 hr.	3.6	10.5	0.05	—	100	0.4
Reflux 2 hr.	3.6	—	—	8.6	100	22.3
Tumble 24 hr.	3.6	—	—	8.6	100	25.3

* Sample went into solution in reaction mixture. Precipitated in methanol, dissolved in chloroform, and reprecipitated.

Gautreaux for the fluidities, Mr. Edmund M. Buras, Jr., under whose leadership this work was initiated, Mr. Austin Mason for fabrication of the glass reaction tubes, and Mrs. Janice P. Evans, Mrs. Julia Sloan, and Miss Margarette Loughlin for physical testing of the yarn.

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The Heat Transmission of Fabrics in Wind

Part II

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Abstract

The thermal transmission of various combinations of fabrics was measured on the hot plate in winds around 17 m.p.h. under conditions simulating to some extent those often present when outdoor clothing is worn in winter. Figures are tabulated which prove that winter overcoats could be immensely improved by use of semineoprene-coated nylon cloth and goosedown for cold windy weather. A conventional winter overcoat for men is shown to be quite inadequate, while the pile fabrics without windproofing are equally disappointing.

Introduction

In a previous communication [6], literature on this subject has been cited; since that time the writer's attention has been drawn to a paper by Nei et al. [5] published in Japan and to a report by Fonseca, Pratt, and Woodcock [1] published in the United States. Nei deals with the effect of cold weather clothing on the skin temperature. Human subjects were used; however, quantitative values in clo units for the clothing were not given. Fonseca, Pratt, and Woodcock deal with the use of the heated cylinder for measuring heat loss in wind.

The problem of heat transfer through clothing resembles to some extent the much less complex one of house insulation, to which science was first systematically applied only about 30 years ago. Today few persons would think of building a house of any great value in the colder parts of North America without giving consideration to the insulation of the walls and to the vapor barriers; yet people are prepared to manufacture, sell, buy, and wear clothing for subzero weather without any idea of its insulating value in figures. Apparatus and information are needed not only to help direct the manufacturer's research program in improving the winter coats he is putting on the market but also to assist the buyer to select a warm coat before he tries it out in cold weather.

Recently the writer has attempted to find a method of test which will do this; such preliminary work

was necessary before approaching the real problem of answering how effective certain combinations of fabrics in cold windy weather might be, what the various combinations weigh per square foot—because after all many fabrics can give adequate insulation if the weight on the shoulders is ignored—how a woven fabric compared with a pile or "fur" fabric, how a pile fabric compared with real fur, and how effective fairly windproof fabrics were. Rough answers to all of these questions are already available without the use of thermocouples and a galvanometer—in fact so much so that if the results on the apparatus were to disagree seriously with the general opinion of the wearing public, the method of test could almost certainly be considered suspect. With this guiding principle in view, this writer concluded, in the work already published [6], that what was under the fabric during test was highly important.

Just as the buyer of house insulation takes into account the fireproofness of a product, so the buyer of winter clothing takes into account appearance and resistance to wear. In selecting the outer materials for the samples used in the present investigation, present-day "wearer acceptability" has been given some consideration; at the same time one must realize that this factor depends largely on current advertising and if a jacket can be produced which gives more insulation for much less weight, it will be accepted by the wearing public regardless of price and appearance for everyday use in severe weather.

Methods and Results

Apparatus

The hot plate and wind tunnel used in the work have been described [7]; measurements in wind in the present investigation were always made with air flow striking at 45°. In order to facilitate the changing of samples and avoid the troublesome task of preventing air from blowing under the sample, two frames of 1¼-in. angle iron, which fitted into each other, were constructed. The lower one was fixed to the mounting of the hot plate with wood screws, while the upper one, lying on the edges of the sample, was drawn down to the lower frame with thumb screws. In this way the edges of the sample were literally clamped between two iron frames.

Tests were generally conducted over two layers of gray flannel regardless of whether an air space was used directly under the sample or not. Two layers of flannel give approximately the amount of insulation worn indoors. Figure 1 indicates in fact that this amount of clothing measured slightly more than one clo unit—the unit of insulation which Gagge, Burton, and Bazett [2] originally proposed for this sort of work. It is described by them as the amount of insulation necessary to maintain in comfort a sitting–resting subject in a normally ventilated room (air movement 20 ft./min. or 10 cm./sec.) at a temperature of 70° F. (21° C.) and a humidity under 50%. In units used in physics and engineering, the clo is equal to

$$0.18 \frac{^\circ \text{C.}}{\text{Cal./hr./sq. meter}}$$

or

$$0.88 \frac{^\circ \text{F.}}{\text{B.T.U./hr./sq. ft.}}$$

Figure 1 also shows that the surface-to-surface value of each layer of gray flannel was only about 0.17 clo; the air in a still air test gives so much insulation that it is more important than the clothing worn when the total insulation is around 1 clo. Gagge et al. [2] give a value of 0.78 clo for air insulation at 20 ft./min. air movement. Our values

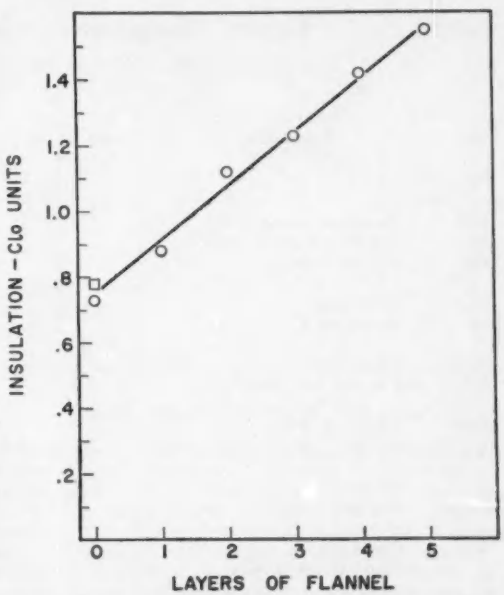

Fig. 1. Insulation of gray flannel spread flat on hot plate—including air resistance. ○, Niven; □, Gagge et al.

for the flannel samples give an intercept on the axis of clo values which fits in satisfactorily with this value. A value of 1.5 clo seems low for the insulation of five layers of gray flannel, because when five layers are actually worn, air is usually pocketed between them; an insulation value would be expected which would be higher than that found when the layers lie flat on each other on the hot plate. This leads to the rather difficult matter of imitating pouching on a hot plate. The writer found that the metal grid which had been used [6] was unsatisfactory when insulations around 4 clo had to be measured, presumably because the metal conducted heat laterally and upset the working of the guard ring. This grid was accordingly replaced by a pad of folded thin string minnow netting ($\frac{1}{4}$ in. mesh, 0.033 in. thick). When folded to give nine layers of netting, the thickness of the pad was about $\frac{3}{8}$ in. Air could pass through the meshes, while the fabric bulged out from the plate during the test.

TABLE I. Some Pertinent Information on the Materials Used in the Samples

Material	Wt., oz./sq. ft.	Thickness, in.	Permeability, cu. ft./sq. ft./min.	Insulation, clo units
Neoprene-coated nylon	0.39	0.0054	0	
Semineoprene-coated nylon	0.24	0.0041	4	
Uncoated nylon	0.28	0.0061	12	
Heavy twill	0.90	0.0172	10	
Gray twill	0.82	0.0168	21	
Millium	0.41	0.0071	14	
Wateline	0.70	(0.25–0.4)	466	1.3
Urethane	1.01	0.5	9	1.9
Batting	1.66	(0.3–0.4)	120	1.5
Goosedown	1.76	(1.1–1.25)	16	4.4
Furleen	1.95	(0.4)	154	1.4
Cloud No. 9	2.14	(0.4)	17	
Elysian navy blue o'coating	2.14	0.166	71	
Frieze o'coating	2.83	0.117	33	
Raccoon fur	3.47	(0.5–1.0)	4	
Beaver fur	3.82	(0.6)	3	

TABLE II. Insulating Effect in Clo Units of Combinations in Wind ca. 17 m.p.h.

Arrangement: cover, SCN when used, insulation, lining, (A) over 2 layers of flannel and (B) over pad of $\frac{1}{4}$ in. mesh netting $\frac{3}{8}$ in. thick and 2 layers of flannel.

Thickness, in. / Insulation / Cover		0 None		0.25–0.4 Wateline		0.3–0.4 Batting		0.5 Urethane		1.1–1.25 Goosedown	
In.		A	B	A	B	A	B	A	B	A	B
.005	Neoprene-coated nylon			1.9	2.9	2.2	3.0	2.5	3.3	4.2	5.4
.004	Semicoated nylon, SCN			1.9	2.8	2.0	2.8	2.4	2.9	4.0	4.4
.006	Uncoated nylon			2.0	2.7	2.1	2.6	2.4	2.7	3.7	3.9
.017	Gray twill			2.0	2.3	2.0	2.3	2.3	2.4	3.6	2.8
.017	Heavy twill			1.9	2.4	2.1	2.5	2.4	2.6	3.9	3.2
.117	Frieze o'coat	1.1	1.7	2.0	2.1	1.9	2.2	2.3	2.5	3.3	2.0
	Frieze o'coat + SCN	1.1	2.0	2.1	2.8	2.2	2.7	2.6	3.1	4.1	4.6
.166	Elysian o'coat	1.4	1.7	2.2	2.0	1.6	1.9	2.8	2.5	3.7	2.6
	Elysian o'coat + SCN	1.4	2.2	2.5	3.1	2.5	3.0	2.9	3.4	4.4	4.8
.4	Furleen	1.3	1.7	2.1	1.8	2.1	1.8	2.8	2.3	3.8	2.1
	Furleen + SCN	1.5	2.2	2.2	3.0	2.5	3.1	2.9	3.2	4.4	4.8
.4	Cloud No. 9	1.7	2.1	2.4	2.4	2.4	2.3	2.8	2.7	3.9	2.6
	Cloud No. 9 + SCN	1.7	2.4	2.6	3.3	2.7	3.1	3.1	3.4	4.5	4.9
.6	Beaver fur	2.7	3.5	3.9	4.3						
.5–1.0	Raccoon fur	3.3	3.9	3.9	4.8						

When the pad of netting was under the sample during a test, conditions simulated those around the chest when a coat is worn with a belt, the neck closed with a muffler or tight-fitting collar, and the front well buttoned or zippered. Tests without the pad simulated conditions across the shoulders where the coat lies tight against the wearer. But still another condition arises when a coat hangs loose on the wearer and air, blowing through porous fabrics, can escape freely downwards. These conditions cannot be simulated on the hot plate satisfactorily and probably need the copperman type of apparatus and tailored samples.

The present investigation deals only with tests on the hot plate with and without the pad of netting. A wind velocity of 17 m.p.h. was about as high as the fan could deliver; velocities only a few miles per hour higher were accompanied by damaging vibrations in the machinery. Figure 2 shows that little further information of value would have been obtained at higher speeds.

A Schiefer-Boyland [8] instrument was employed to measure air permeability using a pressure drop across the sample of 0.5 in. of water. The thickness of most of the materials was measured in a standard thickness-measuring apparatus which normally operated with a weight of 11.31 oz. over a 3-in. diameter disc. Since this pressure was too great for soft materials, an approximate estimate of their thicknesses was made with a common ruler using no pressure—such values are enclosed in parentheses in Table I.

Surface-to-surface insulation values in still air for the materials used as inner insulation are given in Table I. These values were obtained with the "cold side" thermocouple, located under a light blackened aluminium sheet which rested on the top of the sample instead of its usual position in air about 3 in. above the sample.

Description of Samples and Individual Materials

A sample, as distinct from a material, consisted in general of lining, insulation, wind-break, and covering. In certain cases one or more of these items could be omitted; for instance, no wind-break was needed when fur constituted the covering.

The material used for the lining was "Millium," which has a black silky sheen on one side and a gray appearance on the other. The gray side in every test faced away from the hot plate and was always in contact with some other material. Four materials were used for insulation: batting, "Wateline," "Urethane," and goosedown. The batting was cellulose acetate, quilted between two pieces of light canvas. The "Wateline" was a light-weight fleecy material used to augment the insulation of fur coats; the fleecy part appeared to consist of wool, judging from the smell when it was burned, but the net which held it together appeared to be cotton. The "Urethane" was a new material full of pores almost like sponge rubber, but slightly stiffer; its relatively high permeability suggested that the pores were open cells. Sheets ½-in. thick were used. The goosedown was enclosed between two very thin sheets of nylon net. One sheet of net was first tacked on a wooden frame 1 in. in thickness; the frame was next filled with down and covered with another sheet of

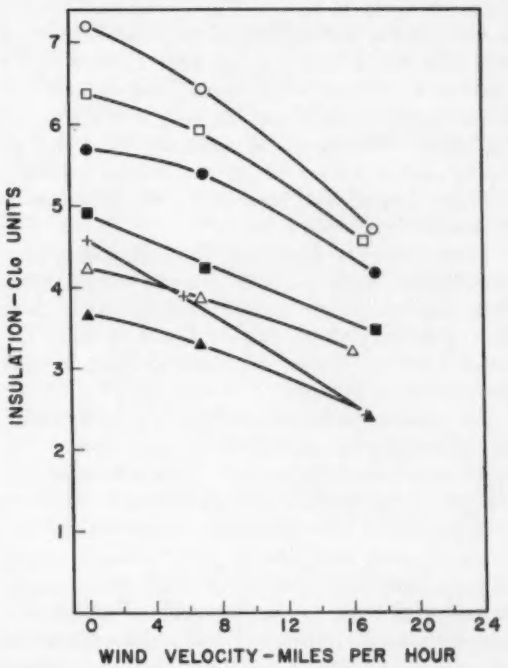

Fig. 2. Graphs illustrating decrease of insulation with increase of wind velocity. ○, 2 layers flannel—netting—Millium—down—s.c. nylon—Cloud No. 9; ●, 2 layers flannel—Millium—down—s.c. nylon—Cloud No. 9; □, 2 layers flannel—netting—Millium—Wateline—raccoon; ■, 2 layers flannel—Millium—Wateline—raccoon; △, 2 layers flannel—netting—Millium—Wateline—s.c. nylon—Cloud No. 9; ▲, 2 layers flannel—Millium—Wateline—s.c. nylon—Cloud No. 9; +, 2 layers flannel—netting—Millium—Wateline—Cloud No. 9.

the nylon net. After the sample was sewn through the down, around the edges, the frame could be removed. When the netting was only lightly drawn in at five points, the insulation of this sample tested under windproof material and including the air insulation was about 7 clo in still air. If the sample was drawn in at points about 2 in. apart on lines about 1¾ in. apart, the insulation dropped to about 6 clo, and when drawn in all along these lines the insulation dropped to 4.4 clo.

This loss of insulation with quilting is of course to be expected; if the down could be kept in place without quilting, it would not only improve the efficiency of the sample but also the appearance, because deep quilting shows through an outer covering. The results reported in Table II which apply to goosedown refer to a sample which was quilted by sewing along lines about 1¾ in. apart. The thickness of this sample was measured from the top of the ridges of the quilting and its surface-to-surface insulation refers to a measurement made with the piece of semicoated nylon spread over it and held down around the edge with the weight of the clamping frame. The blackened aluminum sheet was on top as used in testing the other insulation materials, with the thermocouple between the semicoated nylon cloth and the aluminum sheet.

Three materials were tried for windproofing: uncoated nylon cloth, partially neoprene-coated nylon cloth, and completely neoprene-coated nylon cloth. This cloth was closely woven and was quite different from the nylon net material used to hold the goosedown together.

For covering materials, two furs, two pile fabrics, two overcoatings, and two twills were used. The furs selected were beaver and raccoon because they are two of the warmest [4] of the furs commonly used for coats. For pile fabrics, "Cloud No. 9" and "Furleen" were used, and for overcoatings a sample of best quality navy blue elysian cloth and a sample of dark gray frieze. The two twills consisted of a gray with a silky finish and a drab brown suitable for heavy duty. The "Cloud No. 9" was a pile fabric with a very nice appearance; it has the reputation of being one of the warmest of the fur fabrics. The "Furleen" was included because it had been used in an Antarctic expedition. It is evidently designed to be used as a lining, rather than a covering material, because it is very permeable to air. The navy blue elysian overcoating material was the sort of cloth used for expensive winter overcoats for men; the gray frieze was more the type of material found in a uniform winter jacket for a delivery man.

Measurements

To combine each insulation with each covering material, with and without wind-break, with and without air space (pad of netting), at various velocities, implied a tremendous amount of testing. Furthermore, thermal conductivity tests even under favorable circumstances require much watching and adjusting of electrical currents, and this becomes extremely tedious when samples have high insulation values of 3–5 clo. In order to cut down on the number of tests, the following considerations were taken into account.

1. Results using the completely neoprene-coated nylon were of little interest because wearers who perspire easily will not accept a garment with a perfect vapor barrier; the uncoated nylon was not quite as windproof as the partially coated nylon so there was no need to run tests with it when the treated nylon was available. Thus only one type of wind-break had to be considered.

2. Wind-breaks should not be necessary under furs or twills.

3. Only "Wateline" needed to be used as insulation under the furs, as it was the lightest in weight.

4. Since the insulating value of a coat shows up to poorest advantage in high wind, results at the highest wind speed would give the essential information. (Admittedly there is another problem which concerns a motorist getting into a cold car and waiting till the car heats up; such conditions are not dealt with in the present investigation.)

Figure 2 shows change of insulation with increase of wind velocity. All the graphs have been drawn either straight or curved towards the wind velocity axis. Table II gives some values in clo units in wind ca. 17 m.p.h. The resistances controlling the wind tunnel fan were set at the same setting from day to day; anemometer readings showed, however, that slight changes in wind velocity, sometimes as large as 1 m.p.h., were occurring, due apparently to changes in power supply voltage. Figure 2 shows that slight changes in wind speed can change the measured values by 0.06 clo/mile/hr. While this change in the second decimal place is quite unimportant insofar as the main conclusions of the in-

vestigation are concerned, it can make a change when the first decimal place of the clo value is rounded off to an integral figure. The slight variations in wind velocity have accordingly been considered in drawing up Table II.

Two values are given for each sample under headings A and B; the A values apply to tests made with the sample lying flat on the hot plate with the two layers of flannel underneath and the B values apply to tests made with the pad of netting between the gray flannel and the "Millium" lining of the sample. In all of these tests the two layers of gray flannel—representing "indoor" clothing—were spread directly over the hot plate, and "Millium" was used as a lining for the sample being tested.

The A results can be considered to refer to that small area of a coat which lies tight across the shoulders, and they cannot therefore be taken as realistic values for the respective samples when made up into coats. The B values are in a sense much more realistic, but they depend, unfortunately, on the highly arbitrary pad of netting. That is why the two values must be considered side by side.

The pile fabrics and the men's winter overcoatings were tested without and with a sheet of semicoated nylon cloth directly under the fabric but over any insulation material. Thus for each of these four covering materials there is a quartette of results applying to each insulation material; these four results—with and without wind-break, with and without pouching—should be considered together.

The measurements in Table II were made at entirely different times from those in Figure 2, so that if values at 17 m.p.h. in Figure 2 are compared with the corresponding tabulated values, they will be found to differ by small amounts due to experimental error. To improve on the accuracy of the work might be possible by great elaborations in temperature control of the wind stream or by increasing the temperature of the hot plate very much further above the air temperature; the present results must be considered as only approximate, and when the A value is subtracted from the B value the difference is comparable with the experimental error if the cover is fairly permeable. In spite of this, when the differences are tabulated in Table III, the general trend is quite clear.

By inspection of Tables II and III one can note the following points about the insulation afforded by combinations of the materials in wind.

1. An air space under the sample (pouching, in fact) adds to the total insulation when the outer cover has a low permeability, but if the air permeability of the cover is high the air space may actually reduce the total insulation.

2. Air permeability of the cover is less important without pouching than it is with pouching.

3. Without any insulating lining, the total insulation is always increased by pouching, regardless of whether there is a wind-break under the cover or not.

4. The twills, which are relatively compact and cannot be ruffled in the wind, act as fairly good wind-breaks; since their permeability is appreciable, the total insulation drops when they are substituted for semicoated nylon cloth, in spite of the fact that they are heavier. This deficiency doubtlessly could be corrected by semicoating with neoprene on the inside.

5. The results on the goosedown suggest that it was behaving almost more like an air space than a piece of ordinary porous insulation—at any rate insofar as the permeability of the covering material was concerned. This may be partly due to the presence of fairly large air spaces, resulting from deep quilting.

6. The air permeability of the skin on a fur is low, and in fact compares with that of semicoated nylon cloth; therefore a gain in insulation value is obtained when an air space is added underneath a fur.

The following two measurements could not be conveniently tabulated in Table II because Furleen replaced Millium as the lining. A combination consisting of Furleen–semicoated nylon–Cloud No. 9 measured over two layers of gray flannel and the string netting (wind ca. 17 m.p.h.) yielded a value of 2.8 clo; the addition of Wateline between the Furleen and nylon increased this to 3.6 clo.

Discussion of Results

Values in Table II suggest that the standard winter overcoats sold for men are quite inadequate in subzero windy weather, if 1 clo is needed at a temperature of 70° F. Starting with that assumption [1], if the skin temperature is 92° F., one is led to the conclusion that 1 clo is needed for every 22° F. that the air temperature is below 92° F. (2 clo at 48° F., 3 clo at 26° F., and 4 clo at 4° F.). The metabolism is assumed to be 50 Cal./sq. meter/hr. Admittedly when a man is walking fast his heat

output increases greatly and there are physiological changes under the skin as soon as a man starts to feel cold, so it may be contended that we cannot consider the insulation of a living human being to be equal to the insulation of an inanimate body thermostated at 92° F. surface temperature. Nevertheless, these figures make it clear that 2 clo is wholly inadequate to keep an inactive man comfortably warm for very long if the temperature is even as high as 20° F. (Radiant heat from the sun is not being considered.) The effectiveness of a man's winter overcoat for windy weather could be very considerably improved by completely lining it directly under the outer fabric—but over any inner insulation the coat may have—with the semicoated nylon. A really good winter overcoat could be designed by use of goosedown; however, if this were done the customer would probably find that the nice navy blue elysian cloth was contributing only about half a clo in windy weather and was nearly doubling the weight of the coat.

Results on the fully coated nylon cloth show that complete impermeability of a material over the insulation is desirable from the insulation standpoint. However, a completely impermeable material in a garment can be used only for short periods of time; e.g., when the wearer is waiting for a bus—and the vapor-barrier would have to be opened immediately after. Urethane cannot be considered as an adequate wind-break, and in any case its function is to insulate and the wind-break must be outside of the insulation.

Neither of the fur fabrics measured up to real fur; in fact the Cloud No. 9 was only a little better than a good winter overcoating material and when used over a lining and air space without any windproofing it could rank only with a twill. A very porous variety of fur fabric can actually be inferior to frieze under certain circumstances. The use of semicoated nylon cloth under the fur fabric improves it under certain conditions of test but in no way brings it up to the standard of real fur; additional insulation is required under the nylon. Thus an uninsulated beaver coat compares with a fur fabric coat with semicoated nylon wind break and Wateline for insulation plus Furleen in place of Millium for lining. Data submitted in Table I show that such a combination would weigh more than beaver and Millium per square foot—5.03 vs. 4.23. The comparison with raccoon is worse. The combination Millium–Wateline–nylon–Furleen compares in weight with uninsulated beaver—4.30 vs. 4.23—but the

TABLE III. Change in Insulating Effect, in Clo Units, by Addition of an Air Space (String Net) Between the Lining and the Flannel

Perm.	Permeability Insulation / Textile covers	0 None	9 Urethane	16 Goosedown	120 Batting	466 Wateline
0	Neoprene coated nylon		.8	1.2	.8	1.0
4	Semi coated nylon (SCN)		.5	.4	.8	.9
12	Uncoated nylon		.3	.2	.5	.7
10	Heavy twill		.2	−0.7	.4	.5
21	Gray twill		.1	−0.8	.3	.3
17	Cloud No. 9	.4	−0.1	−1.3	−0.1	0
33	Frieze o'coat	.6	.2	−1.3	.3	.1
71	Elysian o'coat	.3	−0.3	−1.1	.3	−0.2
154	Furleen	.4	−0.5	−1.7	−0.3	−0.3
	Textile covers with wind barrier, or furs					
17, 4	Cloud No. 9, SCN	.7	.3	.4	.4	.7
33, 4	Frieze, SCN	.9	.5	.5	.5	.7
71, 4	Elysian, SCN	.8	.5	.4	.5	.6
154, 4	Furleen, SCN	.7	.3	.4	.6	.8
3	Beaver fur	.8				.4
4	Raccoon fur	.6				.9

insulation of this combination measured 3.0 clo vs. 3.5 clo for the beaver. These comparisons in insulating value all refer to tests over the pad of netting in winds ca. 17 m.p.h.; they indicate that the fabricator of fur fabric coats must go to considerable trouble if his customers are to be satisfied with his wares in windy subzero weather.

However, by use of goosedown a fur fabric coat can be produced which can excel a beaver coat by more than a clo. According to figures taken from Table I, it would weigh 4.36 oz./sq. ft. vs. 4.23 for the beaver. The weight of the goosedown insulation could possibly be cut down by avoiding deep quilting.

The immediate problem is to examine why the fabrics fall short of real fur, and to see how down—either goosedown or eiderdown—can be used to help them compete with and excel real fur in efficiency. In the first place these fur fabrics must be backed with something which makes them only slightly permeable to air if they are to be used as outside materials. This backing does not necessarily have to be a separate fabric like the semicoated nylon used in the tests; it could conceivably be sprayed on. In the second place the pile on these fabrics is shorter than the pile on a beaver pelt even when "sheared." But there may be still a third reason why the fabric falls short of fur; the hair next the skin of a fur is very fine and very dense. To duplicate this condition presents a major problem in manufacturing, and the manufacturers are well aware that it exists [3].

Perhaps as difficult a problem would be the manufacture of a substitute for down; the fibers are branched, and fine streamers emanate from a point apparently in all directions giving a piece of down a three-dimensional character; it will not lie flat like a feather. There seems little doubt that it is the fineness of the fibers coupled with the branched structure that gives the wonderful insulating qualities. By combining this exceptional material with semicoated nylon or any textile which is light and almost windproof, the textile industry can put on the market a product which is both lighter and warmer than fur; for appearance or rough usage a covering material can be added on top if desired, but this adds weight. The first step in putting clothing made of existing textiles on the market which would excel real furs in warmth appears to be to find a method of sticking down together into an insulating mat which could be sold by the yard or else of holding it in place on the garment without deep quilting. If a machine could be developed which would sew through the down without drawing the nylon net in, the deep quilting would be avoided and the surface would be fairly even.

Nylon cloth is a little lighter than Millium, so a slight saving in weight can be made by using nylon as the inner lining. Furthermore, since the insulation of the down dropped from about 7 to 4.4 clo by quilting it is conceivably possible that by an improved method of applying the down to the garment a reduction of weight of 5 oz./sq. ft. could be effected without loss of insulation value. Such considerations suggest that a nylon and goosedown coat could be produced which would be warmer than even an insulated beaver coat and yet weigh 3½ lb. less than an uninsulated beaver coat.

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Letter to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Imparting Wet Crease Resistance to Cotton Fabrics by Cross-Linking with Aqueous Formaldehyde

Southern Regional Research Laboratory[1]
New Orleans 19, Louisiana
May 28, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Although a great amount of work has been done in the last 50 years on reacting cellulose with formaldehyde, it does not appear to be generally recognized that improved wet crease resistance may be imparted with aqueous solutions of this compound without much improvement in dry crease resistance. A recent review [5] makes no mention of producing wet crease resistance with aqueous formaldehyde under conditions where the cellulose reacts in a swollen condition. In view of the current interest in wet crease resistance in certain textile uses, as indicated by the appearance on the market of cotton fabric having this property [1], it may be of interest to report the results of some of the experiments on imparting wet crease resistance with aqueous formaldehyde.

During the course of some work on the cross-linking of cotton cellulose it was observed that reaction with formaldehyde under certain conditions improved wet crease resistance of fabrics without much effect on dry crease resistance. The improved wet crease resistance was observed first on fabric that had been moistened with aqueous formaldehyde, oven dried (or, better, allowed to air dry), and then exposed to the vapor of formic acid in a closed container, preferably about 60° C. Since this method was not suitable for treating large pieces of fabric, at least with the equipment available, other ways were tried. Refluxing the fabric in an aqueous solution of formaldehyde and formic acid produced good wet crease resistance. The effect could be produced by heating the fabric in the solution in a beaker held about 80° C. on a hotplate, or by use of a hooded, steam-heated jig provided with a condenser coil. Ammonium chloride could be used as a catalyst in place of the formic acid, but strength loss appeared to be greater in some instances.

In a typical experiment, a solution composed of 300 ml. of 36% formaldehyde stabilized with methanol, 200 ml. water, and 50 ml. 90% formic acid was used. A strip of commercially mercerized broadcloth, 26 g., and a strip of bleached broadcloth, 26 g., were placed in the solution contained in a 2-l. beaker covered with a watch glass and held at a low simmer, about 80° C., for 6 hr. Loss of volume was replaced with small additions of water. In another experiment, 80 × 80 mercerized print cloth was treated similarly for 6 hr. in a solution composed of 250 ml. of 36% formaldehyde, 250 ml. water, and 0.5 g. ammonium chloride. The fabrics were washed thoroughly in running tap water and air dried. The results are given in the first three lines of Table I.

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I. Effect of Aqueous Formaldehyde on Cotton Fabrics

Fabric	Catalyst	CH_2O content of treated fabric, %	Breaking strength, warp, lb.		Elmendorf tear strength, warp, lb.		Crease angle, W + F, degrees			
							Wet*		Dry†	
			Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated
Bleached broadcloth	Formic acid	0.42	44.0	80.2	1.3	1.9	248	168	197	178
Mercerized broadcloth	Formic acid	0.42	48.5	78.0	1.2	1.8	260	171	168	151
Mercerized print cloth	NH_4Cl	0.24	36.4	47.6	1.7	2.4	273	203	200	197
Bleached broadcloth	Formic acid	0.13	65.0	78.8	1.4	1.7	218	176	180	165

* Method of Lawrence and Phillips [2].
† Monsanto crease angle test.

It will be noted that the wet crease recovery angles are good, although not quite as high as was observed (279° W + F) with a commercially obtained fabric having wet crease resistance imparted by a difunctional etherification agent under alkaline conditions [1, 4]. The improved wet crease resistance of the formaldehyde treated fabrics could also be readily demonstrated by hand crumpling of the wet fabric in water. Although the losses in tensile strength were large, similar losses are tolerated with some commercially used resin treatments. A similar experiment was also made with the same broadcloth fabrics, but substituting 2 g. ammonium chloride for the formic acid. The wet crease recovery angles and formaldehyde contents were nearly the same as obtained with formic acid, but the warp breaking strengths of the treated fabrics were about 9 lb. lower, indicating that formic acid may be better, although more expensive.

In order to see if the reaction could be carried out in a practical way, 50 yd. of 18-in. wide bleached broadcloth was treated on a steam-heated jig. The jig was hooded and vented, with an iced water cooled condenser coil in the vent. The solution was composed of 60 lb. of 37% formaldehyde, 36 lb. water, and 10.5 lb. 90% formic acid. Solution temperature was maintained about 85° C. during the 6-hr. run. The temperature of the vapor in the hood was 60–65° C. Due to excessive losses of volume caused by evaporation through the poorly closed hood and some updraft through the vent to reduce fumes, it was necessary to add 16 l. of a 1 : 1 mixture of 37% formaldehyde and water during the run to maintain volume. At the conclusion of the run, the fabric was washed with cold water, then with hot water and dried on a tenter frame. Its properties are given in the last line of Table I. Hand crumpling in water showed the wet crease resistance of the formaldehyde treated fabric to be improved over the untreated control fabric. The lower average fabric temperature in the jig run probably explains why the improvement in wet crease recovery was less than in the laboratory experiments.

Since it seemed possible that the cross-linking could be carried out at room temperature if a stronger acid was used as the catalyst, a jig run was made on the same bleached broadcloth using a mixture of 50 lb. of commercial 37% formaldehyde and 13 lb. 1 : 1 sulfuric acid. Temperature was about 28° C. for the 3-hr. run. The wet crease recovery angle was 245° (W + F), the warp breaking strength was 55 lb., and the formaldehyde content was 0.83%. Although the process used in this run is similar to that described by Morton in 1941 [3], it is of interest to note that this author stated that no increased resistance to creasing was obtained. It it likely that he evaluated dry crease resistance but did not test for wet crease resistance.

It would appear from these preliminary experiments that further study should be made of the use of aqueous formaldehyde for imparting wet crease resistance to cotton fabrics.

Acknowledgments

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JOHN D. GUTHRIE

The Shape and Cause of Wool Crimp

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June 4, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

A line approximating the actual shape of the crimp of wool fibers can be constructed from arcs of circles and straight lines (Figure 1). The curves are in general made up of arcs of different radii and lengths. Two successive crimps with the same radii are scarcely ever found, while three or more successive crimps of the same radii have never been observed at all. In the case of coarse wools a number of curvatures have been observed which are made up of several arcs in the same direction but with different radii. Straight line portions between the curvatures have been found in wools of all qualities, but mainly in crossbred and coarse wools. However, the alternation of the straight parts and the arcs is irregular, and the length of the straight parts varies.

The crimpiness of the wool fiber is irregular even when the crimps lie in a plane. In spite of the irregularity of the crimp shape, a theoretical regular wave can nevertheless be constructed, the curves and straight parts being obtained by taking the average data of the actual crimps of the wool fiber (Figure 2). Such a theoretical wave constructed from the average data of real crimps, though not corresponding to any of the actual crimps, is characteristic of the type of wool in question.

The following relations are valid for the eight parameters of the theoretical wave:

$$\gamma = 90° - \beta/2$$
$$\beta = 2\alpha$$
$$l = 2\alpha + \rho\beta$$
$$\frac{\lambda}{2} = 2a\cos\alpha + 2\rho\sin\frac{\beta}{2}$$
$$e = 2\rho\cos\gamma$$

Thus, knowing any three of the data, one can fully define the wave.

To characterize the wave we have chosen those parameters where the measurement of the average is the simplest:

$$\rho, \frac{1}{\lambda}, \text{ and } h \text{ all equal to } \left(\frac{l}{\lambda} - 1\right)$$

To characterize fibers which have a three-dimensional form of crimp, and this is frequently the case in crossbred and coarse wools, two projections were plotted on mutually perpendicular planes, intersecting along the longitudinal axis. The projections of both directions are made up of arcs and straight lines following the same principles as for the fibers displaying planar crimp. In the case of wool fibers with three-dimensional crimp the crimpiness of the wool fiber may be characterized by a theoretical space curve, the projections of which on the two perpendicular planes correspond to the scheme given above.

The corresponding data for the projections formed on the two planes need not be identical, and actually are not identical in the large majority of cases.

Thus the crimpiness of a three-dimensionally curved fiber may be defined using the same parameters as that of the planar one, except that two sets of data must be given for each parameter, i.e., the data corresponding to the projection on each of the two mutually perpendicular planes.

Average measurements on Hungarian Transdanubian combed wool of various qualities have been plotted and expressed as a function of the wool diameter. Thus lines have been obtained which are

approximately represented by the following expressions:

$$\rho = 0.267\,d - 2.107$$

$$\frac{1}{\lambda} = \frac{60}{d - 7}$$

$$h = (0.01586\,d - 0.2746) \times 100$$

The numerical values in the expressions are naturally valid only for the Hungarian Transdanubian combed wools tested in our experiments, and it is indeed very likely that they will differ for other types of wool.

Hungarian Transdanubian combed wool of AAA quality has been placed in rooms of differing relative humidity; the number of crimps per unit length of the fiber axis were then counted (Figure 3). The values of h measured as a function of relative humidity and those for I are shown in Figures 4 and 5 respectively. I represents the number of crimps per unit length of the fiber, and is half the number of inflection points. We [4] have obtained relations of the same kind when comparing $1/\lambda$ and h as well as I with the water absorbed instead of relative humidity. Thus, all these relationships show a definite change in the same sense under the influence of either relative humidity or adsorbed water.

Crimpiness is not a constant property of wool fibers, since it is generally increased by conditions hindering swelling or promoting contraction, while

Fig. 1. Reproductions of the projection of wool fibers constructed from arcs and straight lines. Broken lines mark the parts where the plane of the original wave was not parallel with its projection, i.e., where the projection is distorted. Heavy lines mark the straight fiber parts. The sides of angles are drawn with dotted lines. a = curve corresponding to AAA grade wool fibers, b = A grade, c = B grade, d = C grade, and e = E grade fibers.

conditions generally promoting swelling or hindering contraction decrease the crimpiness.

The curves for

$$1/\lambda = f(H_r) \text{ and } 1/\lambda = F(H_2O_{ads})$$

may be geometrically divided into two components (Figure 6), one of which resembles the curve showing normal swelling, while the other is like the one illustrating the reciprocal of the swelling and is connected with an increase of the internal area. Accordingly, we suggest that the curves indicate that it is very likely that the crimpiness of the wool fibers is directly proportional to the swelling of one part of the cortex, while inversely proportional to the swelling of the other one. In other words, the crimpiness of the wool fiber is caused or increased by the shrinkage of one part of the cortex and the swelling of another one.

The part for which the swelling is inversely proportional to the crimpiness is the one which swells with the increase of the internal area, i.e., the layer of higher orientation. It is evident that only substances of higher orientation can undergo swelling with the increase of the internal area, while a simple swelling may be found in the case of substances of lower orientation.

Such a difference of orientation between the two cortical segments has already been pointed out by Mercer [3]. His statement may be completed with our suggestion [2] that this difference of the cortical segments is the real cause of the crimpiness inasmuch as it results in the different degree of swelling or shrinking of the two segments.

It is well known that oriented proteins swell anisotropically; i.e., their dimensional change is smaller lengthwise than crosswise. Naturally, the higher the degree of orientation of the segment, the larger is the anisotropy of swelling, and so also is the difference in the dimensional changes produced by swelling. With the swelling of two protein layers oriented to a different degree, the dimensional changes will be different too. If a difference arises between the length of the two cortex segments, since there is no possibility of sliding with respect to one another, a stress is bound to appear. In drying a similar phenomenon occurs in the opposite direction.

As will be seen from the foregoing, when two substantially interdependent protein segments of dif-

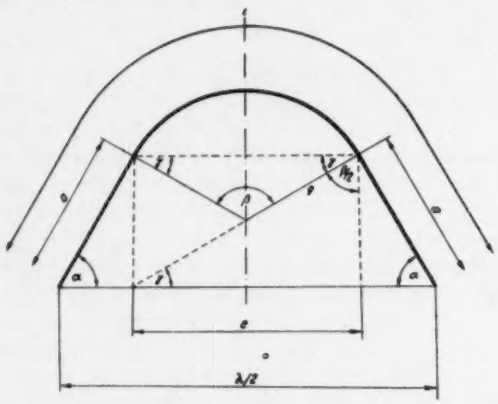

Fig. 2. Theoretical construction for a half wave made up of an arc and two straight lines. $\lambda/2$ = length of one half wave, a = length of the straight parts, α = angle of inclination of the straight parts to the axis, ρ = radius of the arc, β = angle of the arc, l = length of half of the wave line.

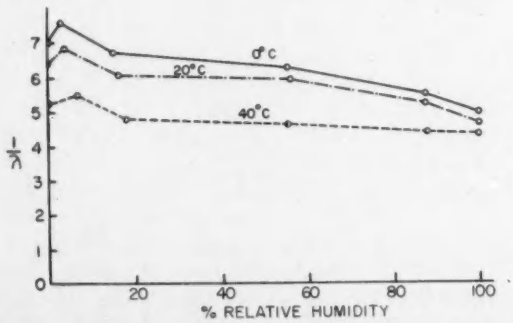

Fig. 3. Diagram of the $1/\lambda = f(H_r)$ relation measured on Hungarian wool grade AAA.

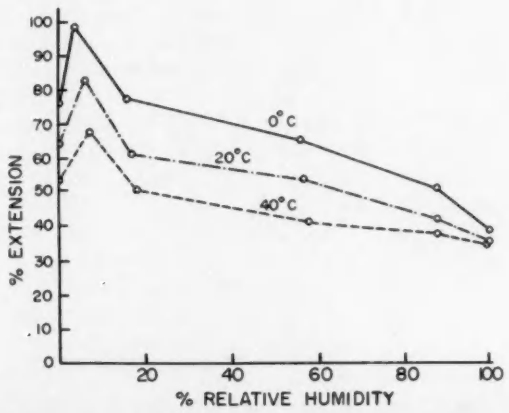

Fig. 4. Elongation during the straightening of the wool fiber, in percentage of the axis length, as a function of the relative humidity.

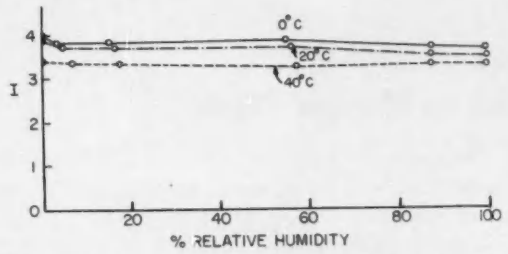

Fig. 5. Change of the *I* number in the Hungarian AAA grade wool as a function of the relative humidity.

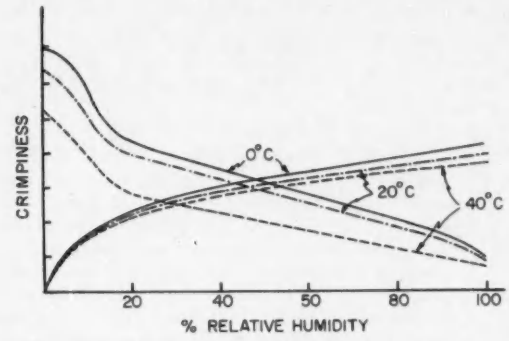

Fig. 6. Breakdown of the $1/\lambda = f(H_r)$ relation measured on Hungarian wool Grade AAA, shown in Figure 3, into its approximate components.

ferent degree of orientation proceed from the original state of swelling to a state of higher or lower degree of swelling, this change will be accompanied by an increase in the difference of length between the two layers; i.e., an internal stress will develop. If a substance with segments of different degrees of orientation—such as a heterogeneous wool cortex—swells or shrinks, stresses will arise between the two segments, causing the bending of the fiber.

The crimpiness of wool fibers will probably be brought about by the internal stresses appearing between the two segments of the cortex as a consequence of the difference of shrinkage in the two segments. This shrinkage occurs in the dehydration of the layers in the course of the biosynthesis. Proof of this is the straightening of the curvature of the fiber when cutting the crimp, since the internal stresses are then abolished or at least reduced. If the para- and orthocortex are neither strictly parallel to one another nor are they lying concentrically but, as in the case of Merino wool, are wound around each other like the singles of a thread, several curvatures of opposite direction will be formed as a result of heterogeneous swelling, and crimps will appear. If the para- and orthocortex are in a parallel position, but are not lying concentrically, a spiral will be formed, as in the hair of Mohair and Karakul goats. Finally, if the fiber is homogeneous or, though heterogeneous yet has a parallel and at the same time concentric position of the para- and orthocortex, the hair is straight.

The conclusion that crimpiness originates from stretched spirals may be true in the case of viscose rayon [1], whereas in the formation of wool crimps, neither stretch nor a spiral shape can be found.

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O. K. DOBOZY

Correspondence Regarding Mosher Paper

Research Laboratory
Purex Corporation, Ltd.
South Gate, California
May 22, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The paper on chlorine retention in resin-treated cottons which was recently published in this journal [1] appears to be a valuable contribution to the subject. Unfortunately, the interesting discussion of possible mechanisms in the introductory section contains sufficient typographical and other errors to warrant comment.

The equation (p. 89) suggested for the hydrolytic degradation of 1,3-bis(hydroxymethyl)-2-imidazolidinone (DMEU) actually depicts a most unlikely hydrogenolysis to a urea derivative. DMEU would be expected to hydrolyze to the unstable carbamic acid I which (see below) would decarboxylate to form the diamine II [3, 4]. The formation of such an amine would probably account for the observed sensitivity of DMEU-treated cottons to hypochlorite bleach.

It seems likely that the troublesome degradation products in fabrics treated with DMEU as well as with other common nitrogenous agents are mainly chloroamines [2] (—C(—)—NCl—), although some chloroamides (—C(=O)—NCl—) are probably involved. The present generally accepted distinction between these two terms is worth maintaining. In the paper under discussion the term "chloroamide" seems to have been used to mean either or both types of structure.

The structure (III) shown [1] for a chloroamide should have been IV or something similar, and that for an amide (V) would be better as VI.

It should be emphasized that these criticisms have no bearing on the validity of the experimental results or on the conclusions which were drawn from them.

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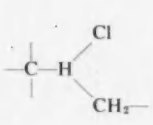
2. *Cf.* Nuessle, A. C., Fineman, M. N., and Heiges, E. O. J., TEXTILE RESEARCH JOURNAL **25**, 32 (1955).
3. *Cf.* Schipper, S. and Day, A. S., "Heterocyclic Compounds," Vol. 5, Elderfield, R. C., editor, New York, Wiley, 252 (1957). By an odd coincidence our copy of this volume contains an equation (p. 384) in which a 2-imidazolidinone appears to be cleaved by alkali to give a urea derivative somewhat similar to the one shown [1]. However, the text makes it clear that the arrow in the equation was accidentally reversed, and that a synthesis of a 2-imidazolidinone is being illustrated.
4. Teramura, K., Niwa, K., and Oda, R., *Chem. Abstr.* **49**, 15734 (1955), have described closely related alcoholysis and aminolysis reactions of DMEU.

ROBERT C. PETTERSON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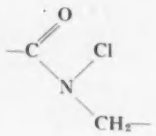
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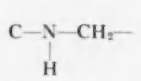
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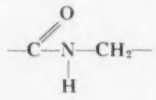
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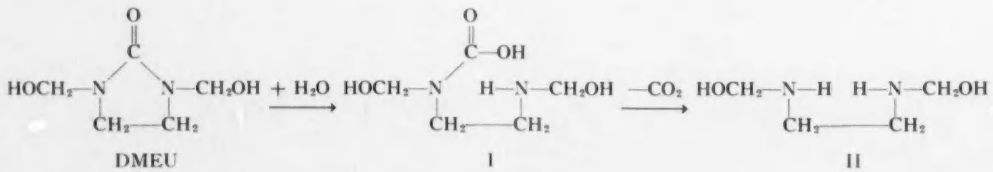

DMEU I II

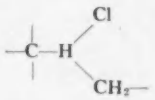
Reply to Petterson Letter

33 Poe Avenue
Newark 6, N. J.
June 6, 1959

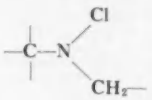
To the Editor
Textile Research Journal

Dear Sir:

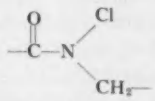
I wish to thank Dr. Petterson for calling my attention to a typographical error that appeared in my paper on Chlorine Retention in Resin-Treated Cotton. The structural formula for a chloroamide, which is represented as



should have been



or, better,



The hydrolytic degradation products of thermosetting formaldehydic condensates affixed on cellulosic fabrics have been more a matter of speculation than chemical demonstration. We find but little evidence of the presence of "dimethylol ethylene diamine" in aged cotton goods finished with DMEU, as suggested by Dr. Petterson.

The troublesome degradation products in fabrics treated with thermosetting formaldehydic nitrogenous condensates and subsequently "chlorine" bleached are, as Dr. Petterson suggests, both chloroamides and chloroamines, although our tests do not confirm his speculation that the latter is the major offender.

H. H. Mosher

An Analysis of Stress-Strain Curves of Soda Treated Wool Fiber

Deutsches Wollforschungsinstitut
an der Technischen Hochschule Aachen
Aachen, Veltmanplatz
Germany
May 21, 1959

To the Editor
Textile Research Journal

Dear Sir:

The changes which occur in wool after mild alkaline pretreatment can be demonstrated by the urea-bisulfite solubility test. Urea-bisulfite solubility decreases proportionately to the time of such pretreatment. Lees and Elsworth [5] suppose that the decrease of solubility is a consequence of the fact that part of the cystine bonds in wool have been transformed into stable lanthionine bonds which are resistant to bisulfite reduction. Thus wool is not soluble in this reagent because the urea only splits hydrogen bonds. Kessler and Zahn [4] also found that raw wool which was washed with organic solvents only followed by treatment with $N/10$ soda solution at a temperature of 45° C. showed a decrease in urea-bisulfite solubility of 17%, whereas untreated wool showed urea-bisulfite solubility of 49%. The cystine content, however, practically remained unchanged (untreated, 12.49%; after 90 min. treatment, 12.25%). During another experiment solubility in urea-bisulfite solution decreased from 55% to 21%, whereas the lanthionine content increased from 0.10% to 0.21% (Kunitz and Zahn [12]).

It is the working hypothesis of Kessler and Zahn that a disulfide exchange in the wool protein takes place during alkaline treatment, whereby intrachenic disulfide groups are being transformed into interchenic disulfide bonds, which causes new cross-links between peptide chains.

An increasing number of cross-linkages between the protein chains in some form or other should become evident in the shape of the stress–strain curve. It is true that various authors [3, 8, 9, 10, 11] have investigated the influence of alkali on the changes in the stress–strain curve of wool. They, however, worked with either stronger alkaline solutions and then merely determined breaking strength or extension at break or, if they used milder alkaline solutions, they investigated the beginning of the stress–strain curves only up to approximately 25–30% extension.

We would rather explain the shape of the stress–strain curve of a wet wool fiber (Figure 1) as follows (*viz.* Peters and Woods [7]).

Within the beginning part of the curve, which is marked by a proportionality between stress and extension (A), preferably intrachenic hydrogen bonds and intrachenic disulfide bonds, the latter mainly present in the amorphous region of the keratin molecule, are effective within the still folded peptide chains. Astbury [1] supposes that the cystine mainly occurs in the amorphous part of the fiber. On the other hand, Bendit [2] proved that an α-β-transformation can already be observed within the first 5% of extension. In higher ranges of extension the intrachenic bonds relax and the peptide chains in the amorphous and crystalline region unfold to the effect that now a larger extension is caused by little adaptation of stress only (Parts B and C of the curve). During this process the polypeptide chains of the crystalline region gradually change into the stretched form. Towards the end of part C and in part D the interchenic disulfide bonds probably are of high importance, since they link together the stretched polypeptide chains, thus diminishing shift-

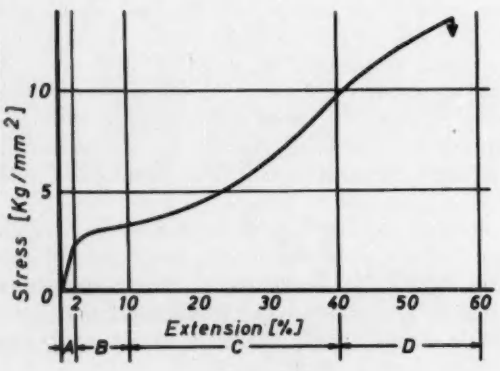


Fig. 1

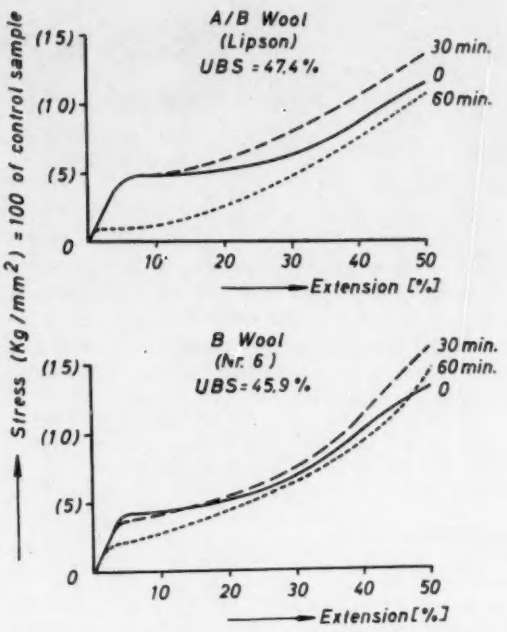


Fig. 2. Wools with a high urea-bisulfite solubility; 0.1 *N* soda pretreatment, 45° C.

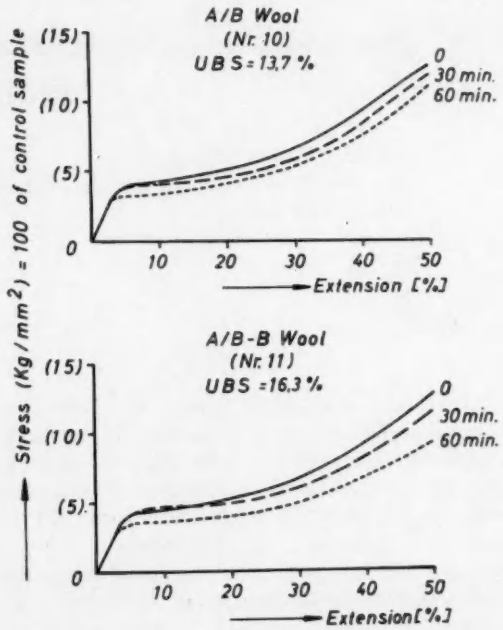


Fig. 3. Wools with a low urea-bisulfite solubility; 0.1 *N* soda pretreatment, 45° C.

ing. Consequently they can stand more stress. An application of corresponding conceptions on a cyclical peptide model dates from Lindley [6].

Generally speaking, we may assume that at the beginning of the stress–strain curve mainly the intrachenic bonds are effective, whereas towards the end the interchenic bonds are of greater importance.

Provided that the above-mentioned hypothesis of an additional cross-linking of polypeptide chains by mild alkaline treatment is correct, this should become obvious towards the end of the stress–strain curve.

Tests

Two wool samples with a high urea-bisulfite solubility and two wool samples with a low urea-bisulfite solubility were treated for 30 and 60 min. in $N/10$ soda solution at a temperature of 45° C.

Tensile tests (200) were made of each sample with fibers of 10 mm. length. The fibers were wet, and the tests were carried out on an instrument with constant rate of extension. The 200 stress–strain curves thus obtained were checked at 10, 20, 30, 40, and 50% elongation in order to find out the existing stress. We obtained a medium stress for every scope of extension which enabled us to draw the average stress–strain curve.

Figure 2 shows the stress–strain curves of the control sample, of wool after 30 min. treatment, and of wool after 60 min. treatment in soda solution, given in percent of the control sample. The control samples of both treatments showed a high urea-bisulfite solubility.

Figure 3 shows the stress–strain curves of two wool samples which had a lower urea-bisulfite solubility from the very beginning.

Soda pretreated wools which already have a high urea-bisulfite solubility before treatment show stress–strain curves which are not parallel to that of our control sample. Either the curves of the soda pretreated wools show higher values towards the end of the curve or, the values being lower at the beginning, the curve resembles that of soda pretreated wool rather than that of our control.

On the other hand, the curves of wools with low urea-bisulfite solubility (Figure 3) run almost parallel to that of the control after soda pretreatment and partly decrease towards the end. In accordance with the above-mentioned molecular explanation of the stress–strain curve, this increased adaptation of stress above approximately 20% elongation (Figure 2) cannot be explained except for the fact that additional cross-linkages have been formed. Even if we assume that hydrogen bonds are being destroyed by mild alkaline treatment, and this process is reflected in the shorter period of steep increase at the beginning of the curve, this difference is not continued throughout the whole curve, but becomes smaller. The cystine bonds which are broken by the mild alkaline treatment make the steep increase at the beginning of the diagram become shorter. On the other hand, new cross-linkages are being formed, thus effecting the increase in stress towards the end of the curve.

Wools which show a low urea-bisulfite solubility from the very beginning probably already have gone through some alkaline treatment which produced cross-linkages; further alkaline treatment does not lead to the formation of any additional cross-linkages. In this case the breaking up of the hydrogen bonds is chiefly responsible for the shape of the curve. Hydrogen bonds mainly affect the amount of tensile tension in the scope of lower elongation values. Therefore the curve is more or less parallel to that of the untreated fiber.

In view of these facts, it should be regarded as proved that the hypothesis set up by Kessler and Zahn [4] is correct in stating that a stabilizing reaction, which was effected by mild alkaline treatment, can not only be concluded from the lowered urea-bisulfite solubility of the material but can be measured directly by the increase in adaptation of stress in the higher ranges of extension.

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G. Satlow

Interpretation of Results from Small Lot Spinning Tests

The Kendall Company
Cotton Mills Division
Research Laboratories
Paw Creek, North Carolina
March 19, 1959

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a recent report in this Journal, Woo [3] uses the Poisson distribution to calculate a series of "critical values" of spinning end breakage which he then proposes be used to "translate the end breakage values for a limited number of spindles to those expected for a larger number."

The observed number of end breaks during any given number of spindle-hours of operation is the best estimate of the population average. The problem is, then, to determine what confidence can be placed in the observation.

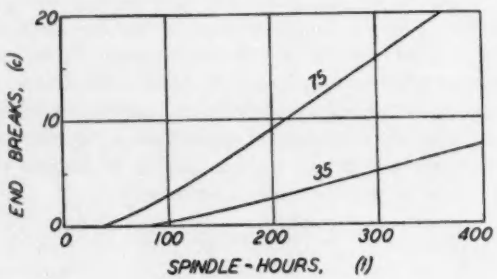

Fig. 1

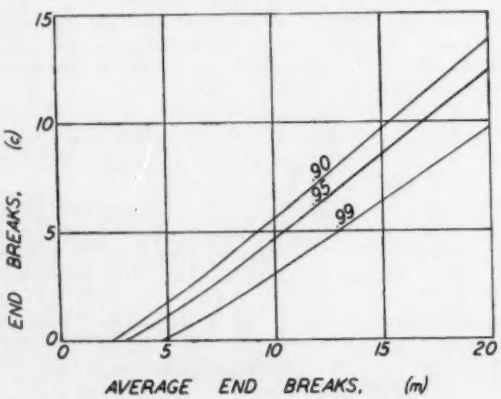

Fig. 2

There are several ways of approaching this problem. Woo shows ([3], Figure 5) "critical values" of end breakage such that the probability of obtaining that number or more of ends down is only 0.05 if the true average is 35 or 75 EDPTSH (ends down per thousand spindle-hours) respectively.

Another way of stating this is: if the number of ends down is equal to or greater than this critical value, the confidence is 95% that the true average is *at least* 35 or 75 EDPTSH.

The labeling of Figure 5 [3] denotes as "good" any experimental result for which its lower confidence limit at 35 EDPTSH has a confidence coefficient less than 0.95. Thus, Woo would classify as "good" an experimental result as high as 60 EDPTSH at 200 spindle-hours (i.e., $c = 12$ breaks).

If an acceptable level of end breakage is assumed, it is more useful to plot end breakage values for which the confidence is 95% that the true average is *less than* this acceptable level.

Using the specific rates of 35 and 75 as Woo does, our Figure 1 shows the maximum number of test breaks c such that the confidence is 95% that the true average is less than 35 and 75 EDPTSH respectively.

The choice of "acceptable" end breakage rates, and the probabilities associated therewith, must be tailored to fit the needs of the mill and test in question. In this respect, limiting a presentation to two arbitrarily selected end breakage rates and a single probability is an undesirable limitation.

The foregoing deficiencies are removed in Figure 2. Here curves are plotted which can be used for any end breakage rate for three confidence coefficients of 0.99, 0.95, and 0.90. That is, these curves are the loci of points meeting the condition

$$\sum_{x=0}^{x=c} e^{-m} m^x / x! = (1 - \beta)$$

In the three curves shown, the values of β used are the three confidence coefficients 0.99, 0.95, and 0.90, but the curves can readily be constructed for others if desired.

To use the curves of Figure 2, one moves horizontally across the graph from the test result, $x = c$, to the intersection with the curve for a selected β. The value of m thus located on the abscissa is inter-

preted as follows: the degree of confidence that the true mean is less than m, when c breaks are observed, is β. A second interpretation is also possible: if m is assumed to be the true mean, any number of observed breaks equal to or less than c may be expected to occur with a probability $(1 - \beta)$.

The information given in Figure 2 may be replotted in a number of ways to suit the desires of the user, but in each, the treatment will lose some element of generality. For example, either or both c and m scales (end breaks) may be replaced by ends down per thousand spindle-hours, R, if the size of the test (t spindle-hours) is arbitrarily held constant. In a similar manner, it may be useful to replace the m scale by size of test, t, as in Figure 1, which can be done if some arbitrary constant rate of end breakage is selected. These changes follow immediately from the relation

$$R_m \cdot t = m \cdot 10^3$$

or

$$R_c \cdot t = c \cdot 10^3$$

It will be noted from both Figures 1 and 2 that the error associated with spinning end breakage tests of 100 or even 200 spindle-hours is so large that the value of a single test of this magnitude has severe limitations. For example, at 200 spindle-hours, the rate of end breakage of the test cannot exceed about 12 EDPTSH and still permit the conclusion, at $\beta = 0.95$, that the true average is less than 35 EDPTSH.

Finally, it is perhaps pertinent to point out that there is no need for extensive computations to plot either Figure 1 or 2 (or Woo's figures). The probabilities are tabulated in various standard references [1, 2]. The reader's attention is also directed to an excellent treatment of this problem by Working [4].

Literature Cited

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3. Woo, H. K. C., Textile Research Journal **28**, 612 (1958).
4. Working, H., "A Guide to Utilization of the Binomial and Poisson Distributions in Industrial Quality Control," Stanford University Press (1943).

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Book Reviews

Cotton. 3rd Edition. Harry Bates Brown and Jacob Osborn Ware. New York, McGraw-Hill, 1958. ix + 566 pages. Price $12.00.

Reviewed by L. Rebenfeld, Textile Research Institute, Princeton, New Jersey

According to the preface it is the purpose of this third edition to incorporate information which was not available when the second edition was published in 1938. Certainly the past two decades have witnessed revolutionary changes in the cotton industry. These changes touch upon all parts of the cotton industry, ranging from the use of modern methods of breeding to the development of delicate final textile finishing operations. The emphasis in this book is heavily placed on cotton fiber production; textile manufacturing aspects are only briefly considered. The many ramifications of breeding, production, taxonomy, chemistry and morphology of cotton, effects of environmental and soil conditions, cotton diseases, and insects are thoroughly treated in this excellent treatise. The economic aspects of cotton trading and marketing are dealt with in two chapters.

References to the original literature and other books are given at the end of each chapter, of which there are 25. A detailed index, which appears to be well cross-indexed, concludes this very worthwhile addition to any cotton technology library.

The Kinetics of Vinyl Polymerization by Radical Mechanisms. C. H. Bamford, W. G. Barb, A. D. Jenkins, P. F. Onyon. New York, Academic Press, 1958. 318 pages. Price $8.80.

Reviewed by Hillary Robinette, Jr., President, Robinette Research Laboratories, Inc., Ardmore, Pennsylvania

An examination of "The Kinetics of Vinyl Polymerization by Radical Mechanisms" indicates that Dr. Bamford and co-authors have treated a particular branch of polymer chemistry in a thorough fashion.

Chapters I and II contain the derivations of the relevant kinetic equations and describe the determinations of individual rate constants. Chapter III is devoted to a treatment of the kinetics of polymerizations of styrene, methyl methacrylate, and other monomers. Chapter IV treats free radical heterogeneous polymerizations with a detailed account of polymerizations of liquid monomers under conditions leading to the precipitation of polymers. It includes an authoritative summary of acrylonitrile polymerization. Chapter V comprises a theoretical treatment of copolymerization. Chapter VI describes the kinetics of initiation, transfer, inhibition, and retardation. Chapter VII, the final chapter, is concerned with size distribution in homopolymers and copolymers and with composition distribution in copolymerization. Relationships between limiting viscosity number and molecular weight distribution, cross-linking, and gelation are also examined.

The volume should prove helpful to students and specialists in radical polymerizations.

An adequate subject index is included; the book is well bound and attractive.

Saco-Lowell Handbook, Engineering and Technical Data, Vol. 4, Fifth Edition. Boston, Saco-Lowell Shops, 60 Batterymarch Street, 1958. 503 pages. Price $15.00.

Designed primarily to furnish technical information relating to the various machines and equipment (their installation, operation, and maintenance) manufactured by Saco-Lowell Shops for the textile industry, this handbook is exceptionally comprehensive. In this respect it is difficult to find any needed information that has been omitted. In addition, some 90 pages are devoted to the presentation, principally in tables, of mathematical data, fiber and yarn information, and electrical and power data. This reference information, ordinarily widely scattered in various handbooks and published literature, adds much to its value. The Handbook, replete with photographs and diagrams, is fully up to date. It is in loose-leaf form and is planned to be kept up to date by the insertion of new or revised pages to be issued from time to time.

Chemie der Azofarbstoffe. (The Chemistry of Azo Compounds). H. Zollinger. Basle and Stuttgart, Birkhäuser Verlag, 1958. 308 pages. Price $9.10.

Reviewed by Emery I. Valko, Lowell Technological Institute, Lowell, Mass.

It was one hundred years ago that Peter Griess discovered the azo compounds. Azo dyes still comprise the largest volume of dyes used. The newest type of dyes, the fiber reactive dyes which promise to revolutionize the dyeing of cellulosic fibers, are mostly azo dyes. Obviously there is ample reason to justify the appearance of a monograph dealing with the chemistry of azo dyes.

In his preface, the author refers to the close cooperation between industrial and academic research at the turn of the century which resulted in triumphal achievements in the field of azo chemistry; such a cooperation is hardly observable today. With this book the author intends to show the younger generation of chemists that this field still can be the source of enjoyment, enthusiasm, and satisfaction for those who decide to pursue it.

Zollinger, professor at the University of Basle and a member of the Ciba research staff, has certainly succeeded in his endeavor. He thoroughly infused all aspects of his subject with modern theories. The literature references cited in footnotes throughout the text comprise some 1000 publications, yet it is apparent that the author did not look upon his task as that of collecting abstracts. He gives, chapter after chapter, a critical evaluation of the work referred to and a concise summary of the present status of knowledge. This is not an easy way to write a book. It is an obligation which in this instance was assumed and met to a gratifying extent.

The treatment is completely up to date. The structure of reactive dyes, for which there was no disclosure in the literature prior to 1958, is already reported here.

The book appears to be remarkably free from printing errors. The mechanism of the attachment of the 1:1 chrome complexes by chelation of the metal atom with both the protein and the dye referred to on page 252 of the book was first formulated by the reviewer. However, it is understandable that this has been overlooked by the author, since the original paper appeared in a publication of somewhat limited circulation. [*Österr. Chemiker Ztg.* **40** (1937)].

The quality of the printing and binding is excellent.

The value of Zollinger's "Chemistry of Azo Dyes" goes far beyond that of a reference work. It is a pioneering and inspiring contribution to an important chapter of organic and industrial chemistry.

Preparation and Dyeing of Synthetic Fibers. H. N. Schmidlin. Basel, Switzerland, Selbstverlag SVG, 1958. 358 pages. Price $6.00.

Reviewed by Herbert W. Fuhr, Celanese Corporation of America, Charlotte, N. C.

This book contains valuable information concerned with the preparation and dyeing of all the synthetic fibers which were commercially available as of November 1958, with primary emphasis on the practical aspects. However, the author also provides necessary information wherever chemistry is involved in the various processes.

It is often difficult, especially for people in the dyeing and finishing field, to find the desired information on synthetic fibers without consuming an appreciable amount of time searching the literature. The reviewer feels that a book on this subject has not been published in English in which such up-to-date information on an international scope has been compiled. A translation, therefore, would be well justified.

Throughout the book the author gives references to publications, thus providing further sources of information for those interested.

In Chapter I, the author gives a survey of practically all man-made fibers, such as their trade names, name of manufacturers, and chemical classification on a world-wide basis.

Chapter II covers the various procedures required for the preparation of the man-made fibers, such as desizing, scouring, heat-setting, chemical and optical bleaching, singeing, the various procedures required to minimize pilling in use, and machinery available for these procedures in this country and abroad. Various illustrations and photographs of the machines are shown, including the machinery used for high-temperature dyeing available at present.

Chapter III describes the various processes for the dyeing of man-made fibers. Special attention is

given to properties of dyeing accelerants, their chemistry, and their application specified for such fiber classes as polyamides, polyesters, polyacrylonitriles, copolymers, and triacetate. Classes of dyes and their manufacturers and trade names are also given, covering practically all types of dyes for synthetic fibers available as of November 1958.

Dyeing procedures—the general mechanism of dyeings and fastness properties—are described in this chapter for nylon types 6, 66, and 11, polyester fibers, acrylics (including Acrylan, Creslan, Darvan, Dynel, Verel, and Zefran), polyvinylchlorides, and triacetate fibers.

In Chapter IV, the various methods for dyeing blends of synthetics with natural fibers and 100% synthetic blends are outlined. Also, fastness properties and the economical aspects of dyeing these blends are compared in various tables.

In the last chapter, the author describes the various continuous procedures for preparation and dyeing, including resin bonded pigments and such processes as the Thermosol, Vapocol, and Emulsion Padding Process.

For those who read German, this book should be of extreme interest due to its value as a thorough source of new information.

Symbolic Logic and Intelligent Machines. Edmund C. Berkeley. New York, Reinhold Publishing Corporation, 1959. 203 pages. Price $6.50.

Reviewed by Sr. M. Stephanie, Georgian Court College, Lakewood, New Jersey

This is a good semipopular treatment of the subject of symbolic logic—its principles, methods and purposes—and the application of such logic to the programming of what the author calls "intelligent machines." A previous book by the same author had as a subtitle *Machines that Think,* so he is consistent, but one—in particular, this reviewer—might not agree that a machine can be intelligent.

Berkeley writes in simple colorful language, gives excellent examples and comparisons, and discusses specific problems which can be solved by machine. Besides symbolic logic, the book contains chapters on Boolean algebra, small and large computing machines, and the algebra of states and events. A bibliography and index are included.

The book should be useful both to the beginner and to the specialist.

Engineer's Job Directory. Cincinnati, Decision, Inc., 1959. 72 pages. Price $5.00.

Reviewed by Candida Frenking, Textile Research Institute, Princeton, New Jersey

There is much work behind the relatively few pages of this publication, and one lead could make it's rather high price for a booklet of this type well worth it. A thousand firms have been chosen as offering exceptional opportunities for engineers, executives, and scientists. Their addresses, number of employees, and the names of the personnel directors are given in an alphabetical listing. There is a job classification index (85 categories) with firms listed under one or more sections, and a geographical listing by state and city. Also given are locations of foreign offices of U. S. firms, and short listings of firms employing students or teachers during summer vacations.

So much for the advantages. Although in an undertaking of this type it is easier to criticize than do a better job, there are definite weak points to be considered.

First, although 1000 firms are in the alphabetical listing, the job classification and geographical indexes are limited to paid advertisers (only 111). For the others, the information is rather scanty. For every company in the alphabetical listing, only the business office address is given, not those of plants or subsidiaries; for the nonpaying firms, only their main product is given, with no indication of their employee needs. For example, two firms manufacturing the same product might have entirely different ratios of research to production men, and a product listing of "diversified manufacturer" is of no help at all to a prospective applicant.

There are 18 pages of display advertising, and the book concludes with a 7-page pitch for the EJD Resume Service, operated by the publishers, Decision, Inc. All told, the venture seems to be a very good one from the point of view of the publisher, but not such a bargain for the job-seeker. Our suggestion: a Sunday copy of the *New York Times.*